DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

FINAL REPORT

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DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

FINAL REPORT

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This report presents field test results obtained on seven individual units measured at one or more operating conditions with different sources of emissions using an experimental dilution measurement technique. The test results are not necessarily representative of the emissions from the source category, or the typical operation of the specific source tested, and should be interpreted as preliminary measurements from the specific source at the measured operating conditions. Also, the test results should be qualified by carefully considering the limited number of tests, background levels and other data quality issues detailed in this report.

Although the report includes preliminary emission factors generated from these test results, it must be recognized that these emission factors were developed using the experimental dilution measurement technique, not regulatory approved test methods. Emission factors developed with the regulatory approved test methods may be substantially different for specific pollutants. Thus, GE Energy does not support or recommend the use of these emission factors for regulatory purposes, permitting or commercial use. The data in this report may be useful for future

refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors.

The dilution sampling and ambient air methods used in this test to characterize stack emissions were previously applied on stationary combustion sources for research purposes. They are not currently approved by any regulatory agency for demonstrating compliance with existing regulatory limits or standards. Further tests are needed to properly validate these methods for stationary combustion sources, especially for extremely low pollutant concentrations characteristic of gas-fired sources.

The emission factors developed from these tests are source-specific for the time and conditions of this tests (see tables below); therefore, they do not necessarily represent emission factors for typical operation of these specific sources or the general population of similar sources. The emission factors are not representative of combustion turbines, combined cycle plants, duct burners or Diesel particle filters. These emission factors are considered for information only in support of the dilution test method for measurement of fine particulate matter, and the test methods described herein continue to be in the developmental phase. No conclusions may be drawn from use of the dilution test method for pollutants other than fine particulate matter.

SITE ALPHA OPERATING CONDITIONS[(a)]

	Run 1	Run 2	Run 3	Run 4
Heat input, % of capacity	85	90	87	91
NO_X/CO Controls	None	None	None	None

[(a)]Values are based on average heat input values calculated over the 6-hour test run period.

SITE BRAVO OPERATING CONDITIONS [(a)]

	Run 1	Run 2	Run 3	Run 4
GT (Load) (%)	100	100	93	85
Duct Burner	ON	ON	PARTIAL[(b)]	OFF
SCR	ON	ON	ON	ON
Oxidation Catalyst	ON	ON	ON	ON
Power Augmentation	Yes	Yes	Yes	Yes

[(a)]Values are based on average heat input values calculated over the 6-hour test run period.
[(b)]Duct burner was firing during part (~30 min.) of the test run and shutoff during the remainder of the test run.

SITE CHARLIE OPERATING CONDITIONS [(a)]

	Run 1	Run 2	Run 3	Run 4
Heat input, % of capacity	100	98	96	95
SCR	ON	ON	ON	ON

[(a)]Values are based on average heat input values calculated over the 6-hour test run period.

SITE DELTA OPERATING CONDITIONS[(a)]

	Run G1	Run G2	Run G3	Run G4	Run O1	Run O2	Run O3	Run O4
Heat input, % of capacity	37	28	35	39	75	82	80	76
Fuel	NG	NG	NG	NG	No.6 Oil	No.6 Oil	No.6 Oil	No.6 Oil
NO_X/CO Controls	None	None	None	None	None	None	None	None

[(a)]Values are based on average heat input values calculated over the 6-hour test run period.
NG = natural gas

SITE ECHO OPERATING CONDITIONS [(a)]

	Hi-Run 1	Hi-Run 2	Hi-Run 3	Hi-Run 4	Lo-Run 1	Lo Run 2	Lo-Run 3
GT (Load) (%)	100	98	100	100	59	59	59
Duct Burner	OFF	OFF	OFF	OFF	OFF	OFF	OFF
SCR	ON	ON	ON	ON	ON	ON	ON
Oxidation Catalyst	ON	ON	ON	ON	ON	ON	ON

[a]Values are based on average megawatt values calculated over the 6-hour test run period.

SITE FOXTROT OPERATING CONDITIONS[a]

	50-B-Run 1	50-B-Run 2	50-B-Run 3	75-B-Run 1	75-B-Run 2	75-B-Run 3
Engine Load, % of capacity	50	50	50	75	75	75
Fuel	LSDO	LSDO	LSDO	LSDO	LSDO	LSDO
Diesel Particulate Filter	No	No	No	No	No	No

	50-DPF-Run 1	50-DPF-Run 2	50-DPF-Run 3	75-DPF-Run 1	75-DPF-Run 2	75-DPF-Run 3
Engine Load, % of capacity	50	50	50	75	75	75
Fuel	ULSDO	ULSDO	ULSDO	ULSDO	ULSDO	ULSDO
Diesel Particulate Filter	Yes	Yes	Yes	Yes	Yes	Yes

[a]Values are based on average heat input values calculated over the 6-hour test run period.
LSDO = low sulfur Diesel oil; ULSDO = ultra-low sulfur Diesel oil.

SITE GOLF OPERATING CONDITIONS [a]

	Run 1	Run 2	Run 3
GT (Load) (%)	99	99	99
Duct Burner	ON	ON	ON
SCR	ON	ON	ON
Oxidation Catalyst	ON	ON	ON

[a]Values are based on average megawatt values calculated over the 6-hour test run period.

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FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (µm) referred to as PM2.5. PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM2.5 concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM2.5 mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source receptor and source apportionment analysis;

- Identify and characterize PM2.5 precursor compound emissions that can be used in source receptor and source apportionment analysis; and

This report is part of a series of progress, topical and final reports presenting the findings of the program.

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EXECUTIVE SUMMARY

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (μm) referred to as PM2.5. PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM2.5 measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative particulate matter sample from combustion systems for determining PM2.5 emission rate and chemical speciation. Dilution sampling is intended to collect aerosols including those that condense and/or react to form solid or liquid aerosols as the exhaust plume mixes and cools to near-ambient temperature immediately after the stack discharge. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM2.5 National Ambient Air Quality Standards (NAAQS) implementation and streamline the environmental assessment of oil, gas and power production facilities.

The overall goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM2.5 mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analyses.

- Identify and characterize PM2.5 precursor compound emissions that can be used in source-receptor and source apportionment analyses.

This report is the last of a series of progress, topical and final reports presenting the findings of the research program. The research program includes field tests at several different types of gas- and oil-fired combustion sources, pilot-scale tests to help develop an improved measurement technology and methods, and technology transfer activities designed to disseminate results and incorporate scientific peer review into project plans and results. The reports present results and identify issues, procedures, methods and results that can be useful for future studies.

The scope of the project included two main tracks:

- Method Development. Large size and weight restrictions previously precluded application of an existing benchmark dilution sampler design to most stationary sources. Pilot-scale combustion tests were conducted to evaluate the effects of dilution sampling parameters (dilution ratio, residence time) for a variety of stack gas conditions produced by gas, oil, coal and doped gas combustion. The results were used to develop new design specifications for a more compact, lightweight dilution sampler. A new compact dilution sampler was constructed and a measurement protocol suitable for use on stationary sources was developed to characterize the emission rates, chemical speciation and size of primary particles and secondary particle precursors. Preliminary validation tests comparing results from the compact dilution sampler and the existing benchmark design were performed in the field on a Diesel engine and a gas-fired power plant.

- Source Characterization Tests. Dilution sampling measurement methods were applied to seven stationary sources to characterize emission rates and chemical speciation profiles for PM2.5 and gaseous precursors. PM2.5 (and precursor) emission factors and chemical speciation profiles were derived from the test results for gas-fired boilers and steam generators, gas-fired combined cycle and cogeneration power plants, gas-fired process heaters, No. 6 oil-fired boilers, and Diesel engines.

FINDINGS

PM2.5 Emission Characteristics

- PM2.5 Mass. For gas-fired sources, dilution sampling indicates PM2.5 mass emissions are extremely low -- probably near ambient air PM2.5 concentrations in many cases. Such levels are difficult to quantify with high confidence using any of the test methods applied in this program – far below both the estimated minimum detection limit (MDL) and lower quantification limit (LQL) of traditional hot filter/iced impinger methods, and generally between the estimated MDL and LQL of the dilution sampling method. Traditional methods for measuring filterable and condensable particulate matter previously have been shown to be subject to small systematic and random biases (due to sampling artifacts and biases) that are very significant at the extremely low particulate concentrations typical of gas-fired sources. The in-stack PM2.5 MDL and LQL achieved with dilution sampling are far lower than can be achieved by traditional hot filter/iced impinger methods due to the avoidance of such biases and greater analytical sensitivity. Therefore, the PM2.5 concentration in stack gases from gas-fired sources measured using dilution sampling is far lower than that measured by traditional methods. While a degree of systematic and random bias in the dilution sampling measurements remains (primarily due to background PM2.5 in the dilution air), these results for gas-fired sources are considered more representative of actual emissions. PM2.5 mass emissions from No. 6 oil-fired sources and Diesel engines are well above the MDL and LQL of the dilution sampling method. Further work on the dilution sampling method is needed, especially for gas-fired source applications, as further discussed below.

- PM2.5 Speciation. The reconstructed PM2.5 mass (sum of species adjusted for element oxides and organic carbon speciation) for gas-fired sources was typically greater than the measured PM2.5 mass by 25 to as much as 200 percent or more in some cases. For the oil-fired boiler and the Diesel engine, the reconstructed and measured PM2.5 mass are in good agreement (within approximately 10 percent). This implies a significant degree of positive bias in the PM2.5 species measurements for the gas-fired sources. For gas-fired sources, dilution sampling results indicate that the majority of PM2.5 is organic carbon (as defined by the thermal-optical reflectance analytical method using the IMPROVE protocol). However, quality assurance measurements indicate it is likely that the organic carbon fraction is overestimated due to adsorption of volatile organic compounds on the sample and quartz filters. This probably explains the imbalance between actual and reconstructed mass. Because of this imbalance, the speciation profiles are normalized to the reconstructed mass rather than the measured mass.

  Measured semivolatile organic species typically accounted for much less than 5 percent of the organic carbon mass. This indicates the likelihood of either a positive bias in the organic carbon measurement and/or the presence of other organic compounds such as fuel fragments and combustion intermediates that were not quantified. In this test program, the semivolatile organic compound analysis method was optimized for quantification of polycyclic aromatic hydrocarbons (PAH) commensurate with the test

objectives. The results strongly suggest that most of the organic carbon mass is accounted for by species other than PAH. A modified analytical approach is recommended in future tests if the objective is to fully speciate the organic carbon mass.

The PM2.5 speciation profiles for gas-fired sources are not distinctive for source apportionment purposes due to the predominance of organic carbon and high uncertainty resulting from the extremely low concentrations of individual species. Sulfate, elemental carbon, ammonium and other ions and elements are minor components for gas-fired sources. Sulfate is the dominant PM2.5 species for the oil-fired boiler, while elemental carbon dominates for the Diesel engine. The speciation profile for the oil-fired boiler also showed elements consistent with the ash content of the fuel that may provide a distinctive signature.

- Particle Size. The test results for gas-fired units indicate that substantially all of the particulate matter in the stack was smaller than 2.5 micrometers. In-stack cyclones with 10 and 2.5 µm cutpoints were used in most tests; however, the results are generally below the MDL of the acetone rinse procedure used to recover particulate matter collected in the cyclones. Recovery of the internal PM2.5 cyclone in the dilution sampler also did not reveal any detectable deposits of larger particles. Exploratory ultrafine (0.1 µm and smaller) particle measurements revealed that peak number concentrations occurred at a size of approximately 20 nm, indicating the predominance of particles formed by nucleation, and that ultrafine particles accounted for approximately one-third of the total PM2.5 mass, assuming unit density (1 g/cc) for ultrafine particles.

  Particle size and composition measurements for the No. 6 oil-fired boiler test showed that approximately 76 percent of the particle mass is represented by particles smaller than 0.32 µm and that the majority of these are sulfate related. This is reasonable considering the elevated sulfur content of the fuel compared to the other sources tested in this program.

  Diesel engine test results with and without a Diesel particulate filter show ultrafine particle number concentration peaks at 60 to 80 nm and that both total and ultrafine particles were significantly reduced by the Diesel particulate filter. Although some studies by others have suggested that addition of a Diesel particulate filter may increase the number of ultrafine particles in Diesel engine exhaust, this was not observed in these tests. The long residence times characteristic of the dilution samplers used in this study may account for at least part this difference, since the lifetime of ultrafine particles is generally short due to rapid accumulation.

Dilution Sampling Method Readiness

- Systematic and Random Variation (Accuracy and Precision). Tests comparing the compact dilution sampler to an existing benchmark dilution sampler showed that the two samplers yield results that are the same at the 95 percent confidence level. However,

further testing is needed to better quantify systematic and random variation, especially for applications with extremely low (less than approximately 1 to 2 mg/dscm) particulate concentrations. Measurement background levels in the dilution air were found to be significant in some tests relative to stack concentrations for gas-fired sources, indicating the potential for further improvements in the equipment and/or procedures to reduce systematic variation for this application.

- Physical Size and Weight. For determining PM2.5 mass, elements, ions, organic carbon and elemental carbon, the prototype compact sampler and ancillary equipment are in total approximately the same physical size and weight as traditional particulate sampling equipment. Adding speciation modules and instrumentation increases the overall size and weight, but to a lesser extent than the equivalent equipment that would be required to obtain a similar scope of speciation using traditional methods.

- Operation. For this program, the sampler was instrumented and equipped with an off-the-shelf computer data acquisition system. Adjustments to the system were made manually. With further engineering of the instrumentation, software and controls, it should be feasible to simplify operation such that it can be operated by a qualified source test individual.

- Sample Recovery. The loading and recovery of sample filter media using ambient air sampling equipment is significantly less complex than traditional hot filter/iced impinger method equipment, with much less potential for contamination and sample loss in the field. The compact sampler design makes it much easier to clean and recover samples from the interior surfaces compared to the benchmark dilution sampler. However, the acetone rinse procedure used to recover deposits from the probe and sample venturi (adopted from EPA Method 5) lacks sufficient sensitivity for applications with extremely low particulate concentration. Other studies imply that PM2.5 deposits in the probe and sample venturi are negligible, therefore the acetone rinse results were ignored for tests of gas-fired sources.

RECOMMENDATIONS

- Dilution Air Improvements. Purified ambient air currently is used for dilution. The current system utilizes high efficiency particulate arrest (HEPA) and activated carbon filters to remove particles and organic compounds from the ambient air. Nevertheless, background levels of particles and organic compounds in the dilution air frequently proved to be significant for tests of gas-fired sources. Means to reduce background levels in the dilution air should be investigated for gas-fired sources. The removal efficiency and cost-effectiveness of other technologies such as ultra-low penetrating air (ULPA) filters, electrostatic precipitation, condensing heat exchangers, and other technologies should be explored to reduce breakthrough of fine and ultrafine particles. Alternatively, pure compressed gases instead of purified ambient air may be necessary for some applications. If reduction of background levels is not feasible, procedures to correct for

the background levels should be implemented. For example, dilution system blanks could be collected for every test run, using either integrated or instrumental methods, and the results used to correct the stack sample results.

- Probe Recovery Procedures. The acetone rinse and analysis procedure, used to recover and quantify deposits from the sample probe and venturi, needs to be improved or replaced with an alternative procedure to achieve lower background levels for application to gas-fired sources. In addition, probe designs (e.g., adding dilution air at the probe entrance through a section of porous or perforated tube wall) that reduce deposits to negligible levels, thereby eliminating the need to recover deposits from the probe, should be explored.

- Validation for Source Types. The method and equipment should be rigorously validated for measuring PM2.5 mass on different source types, e.g., using EPA Method 301 procedures as a guide. Specifically, a significant number of paired dilution sampler tests are needed to distinguish measurement and process variation for rigorous determination of measurement precision. Generation of reference aerosols with known concentration also is recommended, with quantitative recovery of deposits from the various sections of the sampler, over a range of concentrations also is recommended.

- Validation for Species. Validated ambient air speciation methods were applied to the dilution sampler. Validation literature should be reviewed to determine whether further validation tests are needed to extend the results to sample matrices and concentrations in the diluted source samples. Further evaluation of organic carbon measurements is strongly recommended for low concentration sources i.e. gas combustion. More detailed organic carbon fractions should be reviewed from the current test program to determine if a different analytical protocol is justified.

- PM2.5 Emission Factors and Speciation Profiles. The current population of data for each source category is small, but is considered a good start toward developing robust emission factors and speciation profiles. Because of the small number of units tested (one to three), the emission factors may not be representative of either any individual unit or the entire population of units in each category (although this is frequently a limitation of many published emission factors). The high statistical uncertainty (typically in the range of approximately 40 to more than 100 percent) associated with many of the emission factors highlights the need for more tests to better understand and reduce sources of variability. Because it is likely that the emission factors for gas-fired units derived from these tests include a degree of positive bias due to measurement background levels that were demonstrated in some of the tests, the values may be considered conservatively high. Therefore, these emission factors and speciation profiles should be used with caution. Despite these limitations, the emission factors for gas-fired sources derived from dilution sampling are believed to be more representative than other published emission factors based on traditional methods for these sources (which in some cases may suffer from similar limitations) because of improved accuracy and differences in process configuration. Additional tests within each of the source categories evaluated

in this program are needed after dilution method improvements and validation have been achieved.

1. INTRODUCTION

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (µm) referred to as PM2.5. PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM2.5 measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative PM sample from combustion systems for determining PM2.5 emission rate and chemical speciation. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80 to 90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities. The U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the API jointly funded this project.

PROJECT OVERVIEW

The focus of the project included two main tracks:

- Method Development. A dilution sampler and measurement protocol were developed to characterize the emission rates, chemical speciation and size of primary particles & reactive gases that lead to particle formation by atmospheric chemical reactions. Pilot-scale combustion tests were conducted to evaluate the effects of dilution sampling parameters (dilution ratio, residence time) for a variety of stack gas conditions produced by gas, oil, coal and doped gas combustion. The results were used to develop a new compact dilution sampler design. Preliminary validation tests comparing results from the compact dilution sampler and an existing benchmark design were performed in the field on a Diesel engine and a gas-fired power plant.

- Source Characterization Tests. Dilution sampling measurement methods were applied to seven stationary sources to characterize emission rates and chemical speciation profiles for PM2.5 and gaseous precursors.

The overall schedule for the project was:

- Year 1: Source Characterization (existing benchmark dilution system);

- Year 2: Method development and source characterization (existing and new dilution systems);

- Year 3: Source characterization (new dilution system).

The project approach consisted of six tasks (Figure 1-1):

- Task 1 – Method Definition. The focus of this task was to develop and build a more compact, less costly and portable dilution sampler design – a next generation design capable of producing results comparable to the California Institute of Technology (CalTech) design developed in the late 1980's by Hildemann et al. and later improved by Desert Research Institute (DRI). A series of tests was conducted on a pilot-scale combustor to investigate the effect of dilution sampler design parameters on measured PM2.5 under a wide range of simulated source conditions. A draft test protocol for stationary source dilution sampling was developed and is currently being developed as a consensus standard under ASTM International.

- Task 2 – Source Characterization. This task provided for field tests on seven stationary combustion sources (Table 1-1). Measurements included PM2.5 mass, chemical speciation and particle size using dilution sampling methods. Tests at three sites also included comparison tests using traditional hot filter/iced impinger methods. Six of the units were tested firing gas fuel. One of these six sites also was tested firing No. 6 fuel

oil. A Diesel engine also was tested, with and without a catalytic Diesel particulate filter (DPF).

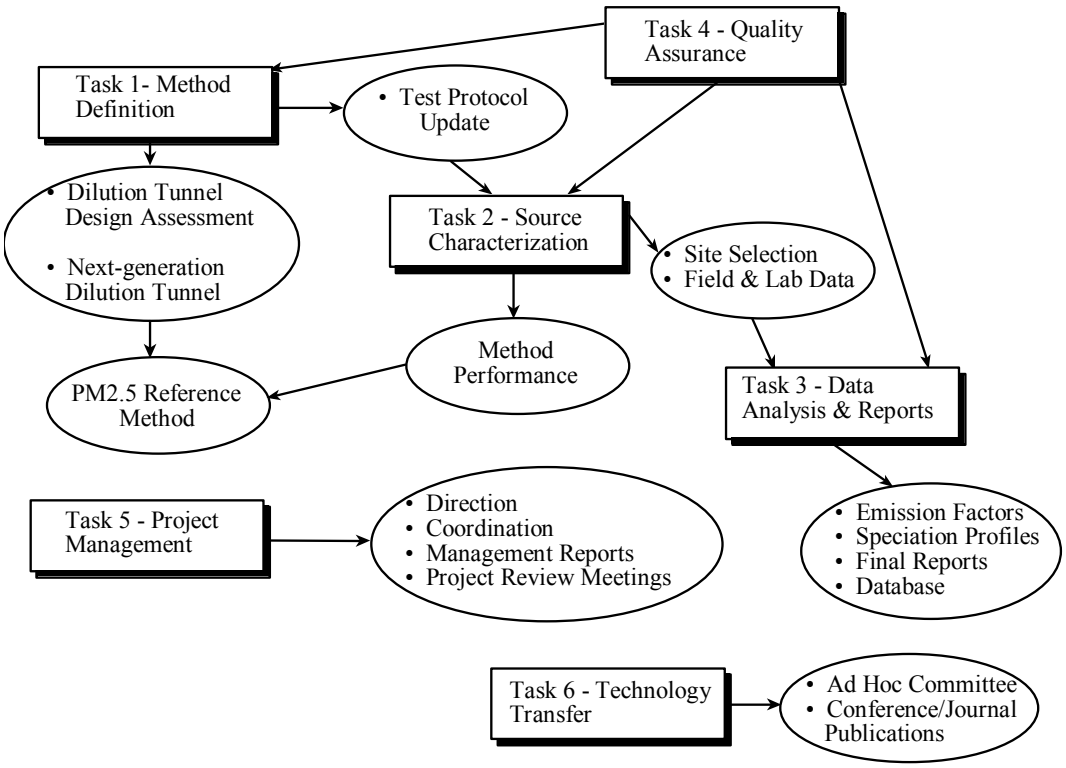


Figure 1-1. Project approach.

Table 1-1. Source Types Tested During Program.

Site Name	Site Description	Dilution Methods	Traditional Methods
Alpha	Refinery Process Heater without NO_X Controls	X	X
Bravo	NGCC with Supplementary Firing and Post Combustion CO and NO_X Controls (heavy duty)	X	X
Charlie	Refinery Process Heater with NO_X Controls	X	X
Delta	Dual-Fuel (Natural Gas and No. 6 Fuel Oil) Fired Institutional Boiler	X	
Echo	NGCC with Post Combustion CO and NO_X Controls (heavy duty)	X	
Foxtrot	Diesel Engine, with and without catalytic Diesel particulate filter	X	
Golf	Refinery Cogeneration Power Plant with Supplementary Firing and Post Combustion CO and NO_X Controls (aeroderivative)	X	

NGCC = natural gas combined cycle power plant

- Task 3 – Data Analysis & Reports. This task provided for reduction of field and laboratory test results and preparation of project reports.

- Task 4 – Quality Assurance. Quality assurance/quality control activities necessary to accomplish this objective were conducted in this task.

- Task 5 – Project Management. Routine technical, budget and schedule management activities were conducted Task 5 (project management reports, technical progress reports, etc.).

- Task 6 – Technology Transfer. For these data to be of greatest benefit, it is important that the results be available in the open literature and that opportunities for peer review of the results are provided. This task provided for conference/journal publications and Ad Hoc Committee meetings of academic, industry, and regulatory agency peers to help guide project direction.

A series of topical and other reports provides detailed project results:

- Update: Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles (Chang and England, 2004a);

- Other Report: Pilot-Scale Dilution Sampler Design and Validation Tests (Laboratory Study) (Chang and England, 2004b);

- Topical Report: Fine Particulate Test Protocol (England and McGrath, 2004).

- Technical Memorandum: Conceptual Model of Sources of Variability in Combustion Turbine particulate with aerodynamic diameter less than 10 µm (PM10) Emissions Data (Lanier and England, 2004);

- Topical Report: Test Results For A Gas-Fired Process Heater (Site Alpha) (Wien, England and Chang, 2003);

- Topical Report: Test Results For A Combined Cycle Power Plant With Supplementary Firing, Oxidation Catalyst And selective catalytic reduction (SCR) At Site Bravo (Wien, England and Chang, 2004a);

- Topical Report: Test Results For A Gas-Fired Process Heater With Selective Catalytic oxides of nitrogen (NO_x) Reduction (Site Charlie) (Wien, England and Chang, 2004b);

- Topical Report: Test Results For A Dual Fuel-Fired Commercial Boiler (Site Delta) (Wien, England and Chang, 2004c);

- Topical Report: Test Results For A Combined Cycle Power Plant With Oxidation Catalyst And SCR At Site Echo (England et al., 2004);

- Topical Report: Test Results For A Diesel Fuel-Fired Compression Ignition Reciprocating Engine With A Diesel Particulate Filter At Site Foxtrot (Hernandez, Nguyen and England, 2004);

- Topical Report: Test Results For A Cogeneration Plant With Supplementary Firing, Oxidation Catalyst And SCR At Site Golf (England and McGrath, 2004b); and

- Topical Report: Impact of Operating Parameters on Fine Particulate Emissions from Natural Gas-Fired Combined Cycle and Cogeneration Power Plants (England, 2004).

REPORT ORGANIZATION

This Final Report provides a comprehensive review of the key project results, organized in the following sections:

- Section 1 – Introduction

- Section 2 – Dilution Method Development

- Section 3 – PM2.5 Emission Factors and Speciation Profiles

- Section 4 –Findings and Recommendations

2. DILUTION METHOD DEVELOPMENT

BACKGROUND

Overview of Stationary Source Dilution Sampling Systems

Dilution sampling has been used for more than 40 years to collect source emission samples for determination of various emission properties. It was adopted as the regulatory standard method for determination of particulate emissions from mobile sources including heavy-duty Diesel engines (International Organization for Standardization – ISO – 8178, 1996a, 1996b; U.S. EPA, 1992). At that time, dilution sampling equipment was bulky, expensive and complex to operate. Testing was done primarily in the lab, which did not pose a problem for routine testing since the mobile source could come to the laboratory. Dilution sampling was considered impractical for routine testing of stationary source emissions where the test equipment must be transported to the field and access to sampling locations on elevated platforms is difficult; therefore, other non-dilution methods based on heated filters (and later the addition of iced aqueous impingers for condensable PM) were adopted by regulatory agencies. Researchers continued to use dilution sampling to develop chemical speciation profiles for stationary sources.

Over the past 20 years, many designs evolved for stationary source sampling. The characteristics of some of these recent designs are summarized in Table 2-1. Many of these designs are discussed in more detail in England et al. (1998) and Chang and England (2004a). Dilution sampling typically involves extracting a sample form the stack or flue, diluting it with purified ambient air or pure compressed gases, then obtaining samples with ambient air collection and analysis methods. In some designs, the sample is aged after mixing to allow additional time for aerosol formation. Because the sample is cooled to ambient temperatures, aerosol formation conditions approximately simulate those in actual exhaust plumes (to the extent practicable) and test results are therefore more directly comparable to ambient air measurement results than are those from hot filter/iced impinger methods.

Table 2-1. Features of Recent Dilution Sampler Designs

System	Tunnel diameter (cm)	Effective mixing length (diameters)	Nominal Residence time (sec)	Dilution ratio	Mixing section Reynolds number	Aging Section Diameter (cm)	Aging section Reynolds number	PM2.5 cut after aging?	Tunnel material	Portability?	References
Carpenter	30	12 to 15	1.3	8:1 to 25:1 typ (up to 100:1)	47,000	N/A	N/A	No	Stainless steel	No	Carpenter (1978)
NEA	10	29	1 to 3	>20:1	11,000-23,000	N/A	N/A	No	PVC	Luggable	Houck et al. (1982)
SRI	21	6	6.2	25:1	2800	N/A	N/A	No	Acrylic and Teflon	Yes	Smith et al. (1982)
CalTech	15	10	2 to 180	40:1 (25:1 to 100:1)	10,000	46	700	Yes	Stainless steel and Teflon	Luggable	Hildemann et al. (1989)
URG	8	8	5 to 40	20:1 to 40:1	na	8	na	Yes	Teflon-coated glass and aluminum	Luggable	URG (1996)
California ARB	15	12	1 to 5	10:1 to 50:1	10,000	N/A	N/A	No	Teflon-coated stainless steel	Yes	Wall (1996); Lindner and Wall (1995)
DRI	15	18	80 typically)	40:1 (25:1 to 50:1)	9,000 (at 40x dilution ratio)	46	700	Yes	Stainless steel	Luggable	
EER	20	1	10	20:1 (10:1 to 40:1)	5500	20	800	Yes	Stainless steel	Yes	Chang and England (2004)
CMU	15	15	0 to 12 minutes	20 to 200	3000-13000	na	na	Yes	Stainless steel	Luggable	Lipsky et al. (2002)
CANMET 1	6	25	20 to 80	40:1 (25:1 to 100:1)	7500 (at 40:1 dilution ratio)	na	650	Yes	Teflon-coated aluminum	Luggable	Lee et al (2002)
CANMET 3	5	40	10 to 40	40:1 (25:1 to 80:1)	13,000	30	1,400	Yes	Teflon-coated stainless steel	Yes	Lee et al (2003)
PAPRICAN	14.5	18	90	30:1 (25:1 to 40:1)	11,000	27	170	Yes	Teflon-caoted stainless steel	Luggable	O'Connor (2003); O'Connor and Genest (2003a, 2003b)
EPA	14	3.2	1	20:1 to 40:1	na	N/A	N/A	No	Teflon-coated aluminum and stainless steel	Yes	U.S. EPA (2003a)

N/A - not applicable
na - data not available

Mobile Source Dilution Systems

Dilution sampling systems have been used for mobile source sampling for many years. The main applications have been type testing of reciprocating engines (gasoline and Diesel) used in automobiles, locomotives, marine vessels, and others (U.S. EPA, 1994; ISO 8178, 1996a, 1996b). Typically, these systems dilute the sample at overall dilution ratios of 10:1 to 50:1 and higher, in one and sometimes two stages of dilution, with rapid sample-dilution air mixing and short total bulk mean gas residence times (typically 1 to 5 seconds) (Figure 2-1). Constant volume sampling is common, where the total exhaust from the engine is captured and diluted, then divided for sampling. There is a large body of literature for mobile and Diesel engine

applications regarding design and use of dilution samplers, and many issues remain controversial. Kittelson (1999) provides an excellent review of recent dilution sampling issues for Diesel engine applications.

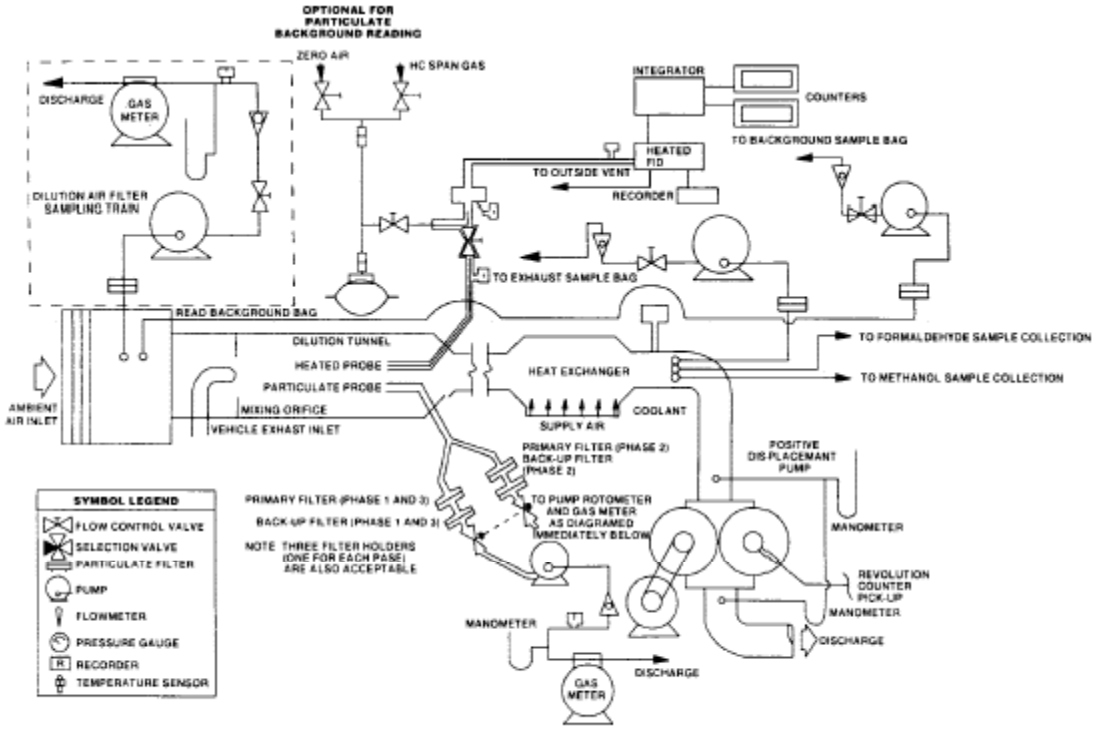


Figure 2-1. Typical Constant Volume Dilution Sampler for Mobile Source Testing (U.S. EPA, 1994).

While the lessons learned from mobile source applications are useful, not all of them may apply directly to stationary sources because of distinct differences in the process and exhaust characteristics. Reciprocating internal combustion engines tend to produce relatively high concentrations of unburned or partially burned fuel fragments, resulting in relatively high concentrations of organic vapors and nanometer-sized soot particles in the exhaust that are usually the main source of particulate emissions from such engines. The residence time in the combustion chambers during the combustion stroke is on the order of milliseconds. Combustion products are then rapidly discharged to the atmosphere (typically much less than one second from combustion chamber to atmosphere) without further heat extraction at relatively high temperatures. Because of the high concentrations of soot and organic vapors and high temperature at the point of discharge, significant changes to aerosol size and number typically

occur rapidly after discharge. These conditions are generally true for both mobile and stationary reciprocating internal combustion engines, although timescales can be slightly longer for stationary reciprocating engines that rotate more slowly and those with post-combustion emission controls.

Many stationary sources are external combustion devices (e.g., boilers, process heaters, etc.), direct combustion devices (kilns, etc.), continuous internal combustion devices (e.g. combustion turbines) and non-combustion processes. Combustion efficiency is a premium for these sources and rarely are large amounts of unburned fuel and soot present in the exhaust under normal "good combustion practice" conditions. Combustion chambers and exhaust gas paths are relatively large, per unit of fuel burned, in comparison to typical mobile reciprocating engines. Residence time at high temperature in external combustion chambers may be on the order of 3 to 5 seconds, enabling combustion to proceed further to completion than reciprocating engines. Heat recovery equipment is frequently used after combustion to extract useful heat, cooling the flue gas to relatively low temperatures and providing additional gas residence time. The total gas-phase residence time prior to discharge in large stationary sources with air pollution control equipment such as electrostatic precipitators and scrubbers may easily exceed 10 seconds. Because of relatively long process residence times, frequently cooler stack temperatures, and lower concentrations of condensable vapors and soot, aerosol dynamics are typically relaxed to a much greater degree for external combustion sources than for reciprocating engines.

Thus, specific dilution sampling parameters that are important for reciprocating engines may be more or less important for stationary external combustion devices and other processes because the time scales from combustion to sample are significantly different. For example, Kittelson (1998) conducted experiments showing that nanoparticle number size distributions in Diesel exhaust change dramatically over time scales from 0.04 to 6 seconds (Figure 2-2) and are very sensitive to dilution ratio, humidity, and temperature of the dilution air. Note, this may not translate directly to dramatic changes in total PM2.5 mass since the smallest particles have the least amount of mass and the simple accumulation of smaller particles into larger ones does not change their total mass. For many stationary combustion systems, the total residence within the process is on the order of 6 seconds; thus, at least some of the changes observed by Kittelson may already have occurred prior to the exhaust sampling point.

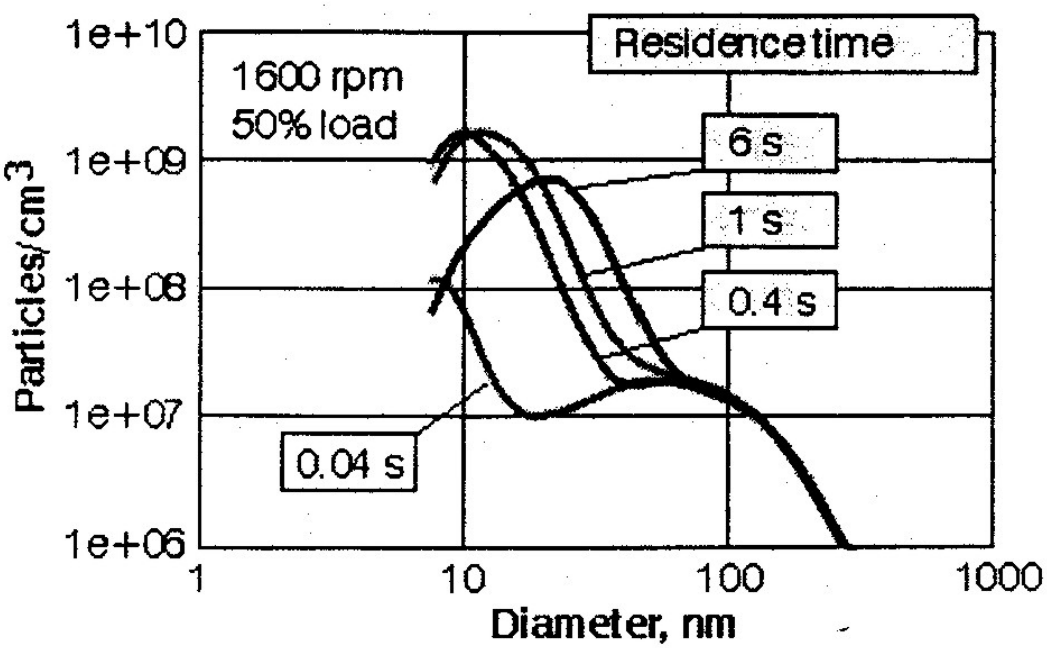


Figure 2-2. Effect of Dilution Sampler Residence Time on Particulate Number Concentration and Size for a Diesel Engine (Kittelson, 1998).

Recent Designs for Stationary Source Sampling

The design developed by Hildemann, Cass and coworkers at CalTech has become the benchmark for sampler design in recent years (Figure 2-3). The unique features of this design, which was developed with an emphasis on characterizing trace organic aerosol profiles, is it's U-shaped mixing tunnel followed by a large aging chamber providing a total residence time of approximately 80-90 seconds. The long residence time was specified to allow dilute organic vapors sufficient time (diffusion limited) to condense into the aerosol phase. Time scales on the order of a few seconds are relevant to mobile source emissions characterization because the time from tailpipe emission to human exposure in traffic is similar. However, the exhaust of most medium to large stationary sources is high above grade and time to human exposure is measured in minutes to hours, or even days. Therefore, longer time scales are more relevant for characterization of stationary source emissions.

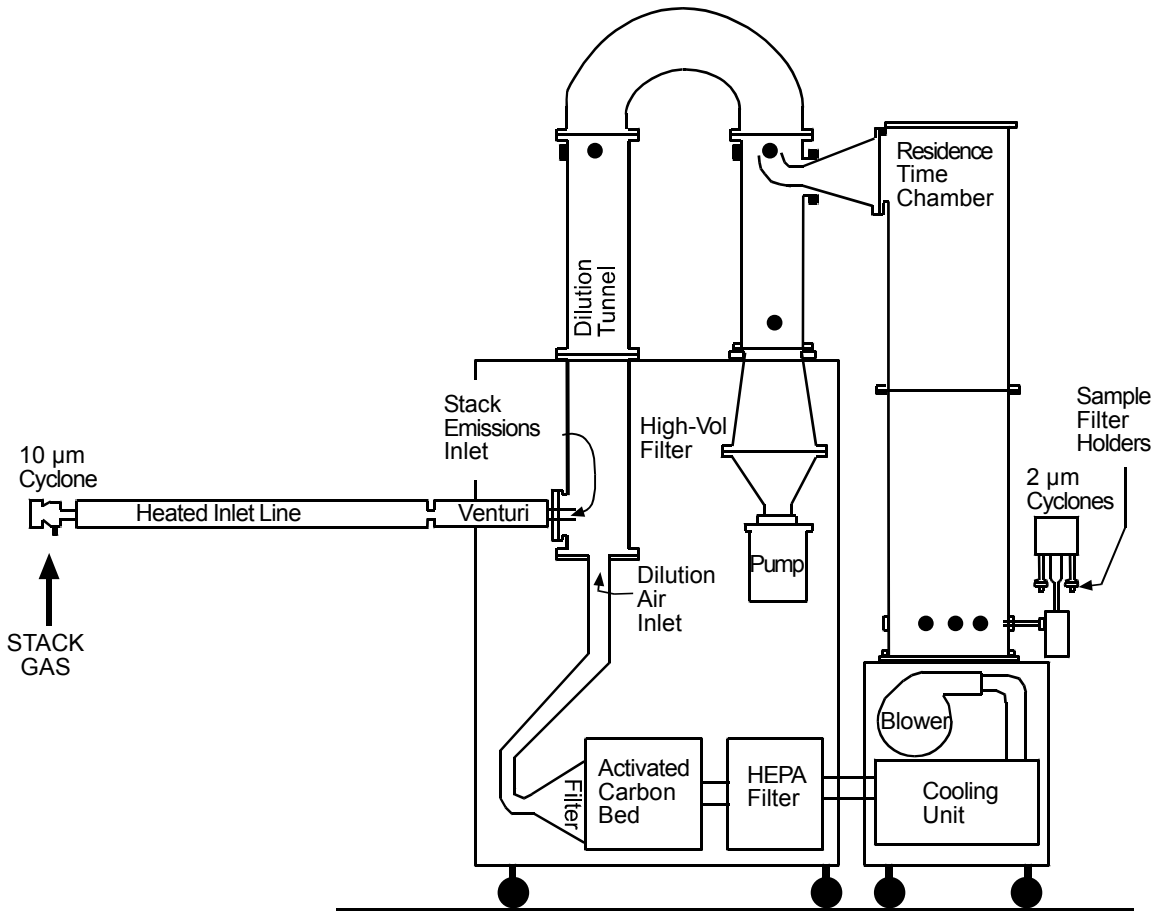


Figure 2-3. CalTech Dilution Sampler (Hildemann et al., 1989).

Hildemann's design is well characterized. One of the key issues is loss of particles within the system prior to the sample collection filters. Hildemann quantitatively characterized particle losses as a function of particle size using monodisperse ammonium fluoroscein particles. Hildemann's results showed that losses of diluted sample in the dilution tunnel and aging chamber are very small, less than 3 percent, and independent of particle size, but that losses of undiluted sample in the probe and venturi could be significant depending on particle size (Figure 2-4). Hildemann's results show that particle losses in the probe plus venturi decrease exponentially with decreasing particle size, with losses falling from 18 percent for 2.4 microns (µm) particles to 5 percent for 1.4 µm particles. Thus, for the size range of interest (PM2.5) in the current program, the maximum potential particle losses in the probe and venturi are expected to be on the order of approximately 18 percent, and probably much less than this because the majority of particles are expected to be much smaller than 2.5 µm. These results imply that the

sample recovery strategy should focus on recovering deposits from the probe and venturi, and that deposits in the dilution tunnel and residence chamber can be neglected.

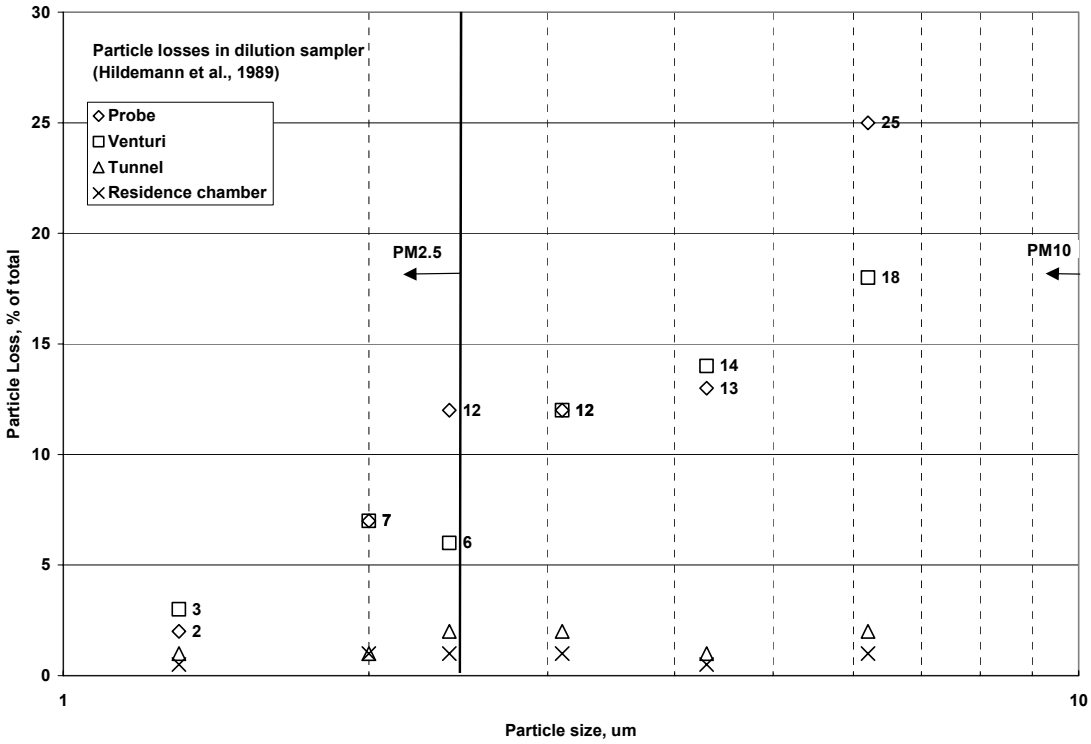


Figure 2-4. Dilution Sampler Particle Losses (from Hildemann et al., 1989).

Many published source emission speciation profiles developed since 1990 have used this and similar designs. In 1996, API commenced a series of tests using a version of the Hildemann sampler developed at DRI (Figure 2-5) on gas-fired refinery process heaters/steam generators and on fluid catalytic cracking units (API, 2001a, 2001b, 2001c). The tests proved the feasibility of applying the DRI dilution sampler to stack sampling of large gas-fired stationary sources, producing new PM2.5 emission and speciation results for these units. Researchers at DRI applied this sampler to coal-fired boil–ers, a refinery fluid catalytic cracking unit and to various smaller area sources such as fireplaces and cooking stoves (Chow et al., 2004; Watson et al., 2002). Lee et al. (2000) and Lee (2001) applied a similar sampler (Figure 2-6) to laboratory combustors firing heavy fuel oil and coal. U.S. EPA researchers applied a similar sampler (Figure 2-7) to characterize wood combustion (Dayton and Bursey, 2001) and Diesel engine exhaust (Miller et al., 1998). O'Connor (2003) and O'Connor and Genest (2003a, 2003b)

applied a similar sampler (Figure 2-8) to pulp and paper industry sources, including sampling in saturated flue gases from several sources equipped with wet flue gas desulfurization scrubbers. Kleeman et al. (2000) applied the Hildemann sampler and Lighty et al. (2000) applied the DRI sampler for characterizing PM from motor vehicle emissions. Thus, the Hildemann et al. sampler design and its derivatives have gained a considerable degree of acceptance among the research community for developing PM2.5 chemical speciation profiles for a broad range of combustion sources.

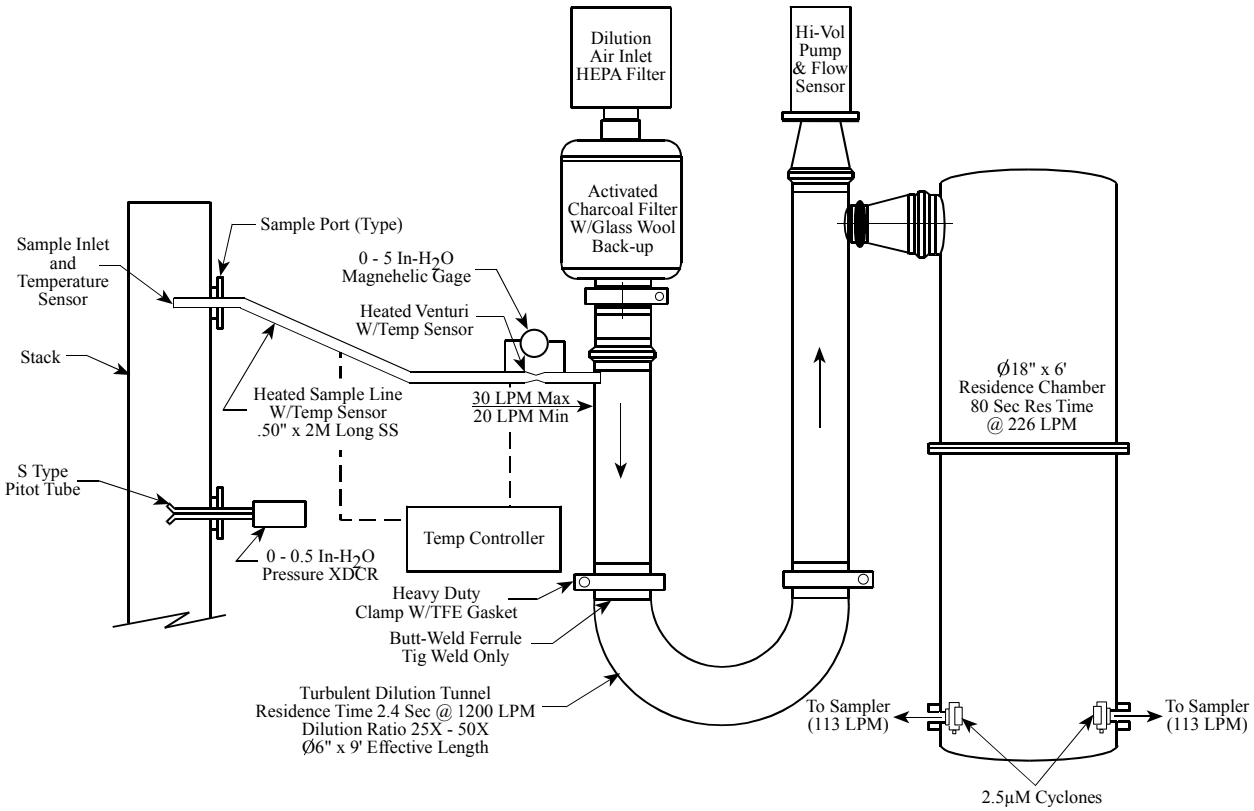


Figure 2-5. DRI Dilution Sampler (Chow et al, 2004).

Dilution sampling technology was selected as the basis for the new test method developed under this program because:

- It is widely accepted in the scientific literature for assessing source contributions to ambient PM2.5;
- For decades it has been the internationally-accepted regulatory reference test method for mobile reciprocating internal combustion engines;

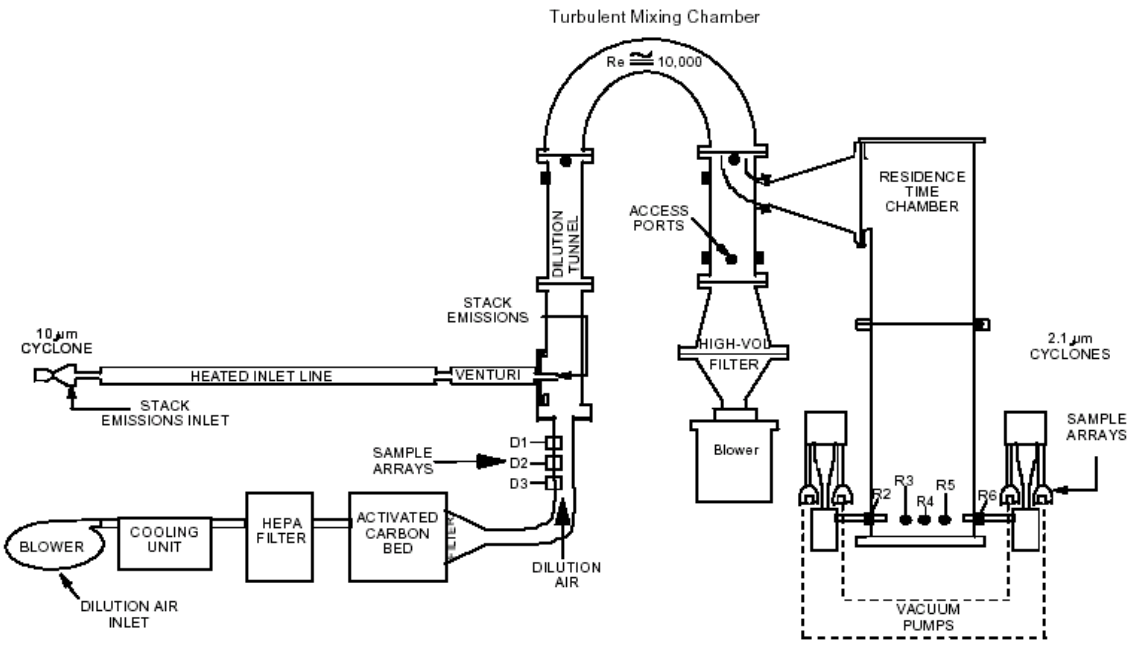


Figure 2-6. U.S. EPA Dilution Sampler (Dayton and Bursey, 2001).

Figure 2-7. CANMET Dilution Sampler Version 3 (Lee et al., 2003).

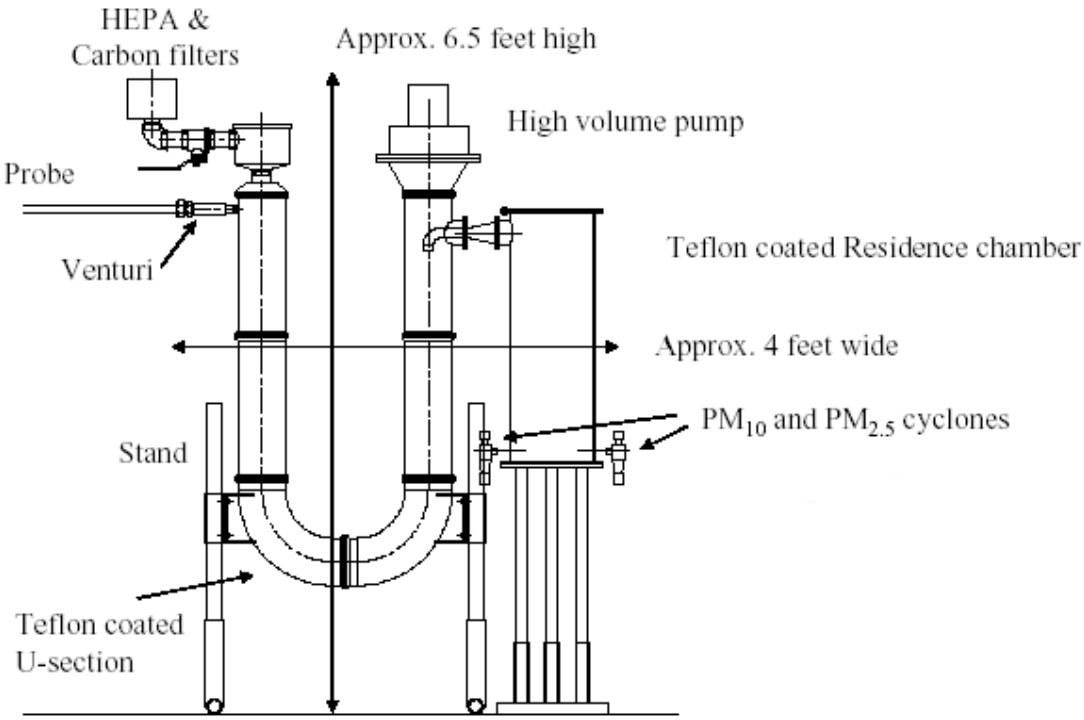


Figure 2-8. PAPRICAN Dilution Sampler (O'Connor, 2003).

- It offers measurements free from significant artifacts associated with current stationary source particulate test methods;

- It provides conditions approximately simulate those in actual exhaust plumes (to the extent practicable), providing a more representative measurement for purposes of PM2.5 source apportionment and human health risk assessments than hot filter/iced impinger methods;

- Compared to current stationary source test methods based on hot filters and impingers, it enables a broader range of chemical and physical characterization and better comparability to ambient PM2.5 measurements through the application of ambient air sample collection and analysis methods;

- It offers potentially improved overall in-stack sensitivity because of improved analytical sensitivity.

In particular, the Hildemann dilution sampler design was selected because of its most unique design feature—a long residence time for aging the aerosol after dilution—for characterizing

organic aerosols. While the Hildemann design has been successfully applied to a limited number of stationary sources, its large physical size and weight make it impractical for the limited space and access available for the majority of stationary source testing situations. Although a variety of designs have been developed for specific applications, the limiting design parameters and operating conditions of dilution samplers—e.g., mixing rate, residence time, dilution ratio, geometry, humidity, etc.—needed to produce representative samples for different fuels and stationary processes are not well established. Therefore, an improved design is needed that is more compact and lightweight yet maintains conditions needed for representative and accurate measurements.

Methods and Procedures

One of the goals of the current program was to use dilution sampling for determining both PM chemical speciation and PM mass emission rates. Previous applications of dilution sampling sought primarily PM chemical speciation profiles. In the current program, it was demonstrated that for some cases both PM mass emission rate and PM chemical speciation are strongly method dependent due largely to problems with the other methods (Wien et al., 2001). In such cases, using PM speciation results obtained from dilution sampling and PM mass emission rates obtained from other methods to estimate speciated emission rates may lead to large errors. Therefore, the sampling procedures applied in this program were designed to quantify both mass and speciation.

Another potential issue when comparing source profiles produced by different researchers is the comparability of the actual sampling and quality assurance/quality control procedures. The dilution sampler procedures used in this program, described in more detail elsewhere (England and McGrath, 2004a), included the following general steps:

Pre-test Procedures:

- Cleaning: During the previous API program, the entire sampler was solvent degreased followed by application of heating tapes to bake-out any residual organics. During bake-out, the unit was heated to 150 ºC and a small flow of purified air was run through the system for four hours. In the current program, solvent degreasing became impractical due to lack of any local facilities capable of handling the size of

the dilution sampler. Therefore, the solvent degreasing procedure was replaced by rinsing all interior surfaces in contact with the sample with distilled deionized (DI) water followed by acetone to remove all visible deposits was adopted. The bake-out procedure remained the same. The high efficiency particulate arrest (HEPA) and activated charcoal filters used to purify the dilution air were baked in an oven at 150 ºC for two to four hours, or occasionally replaced (the capacity and life of the filters is not known at this time, so a replacement schedule has not been established).

- Sample media preparation: This consisted of preparing all the sample media necessary for the specific test (filters, sorbents, etc.) in the laboratory. All filters needed for the test were assembled into filter holders in the laboratory and capped. This eliminated the need to handle the filters themselves in the field, avoiding any contamination or sample loss. Other media for speciated measurements were prepared and stored as required by the various protocols.

- Calibration: Flow elements, pressure transducers, Pitot tubes, relative humidity elements, and thermocouples were calibrated periodically. Venturi flow and orifice elements were calibrated one time, inspected for damage prior to each test, and recalibrated against a new venturi flow element if any visible damage was present. Pitot tubes were dimensionally calibrated prior to each test. Thermal mass flow elements were calibrated by the manufacturer and recalibrated annually (or more frequently if visible deposits or damage was present). Thermocouples were calibrated annually against a mercury-in-glass thermometer. Relative humidity elements and rotameters were factory calibrated.

- Dilution Sampler Configuration and Run Time: The specific configuration of the dilution sampler and ancillary equipment varied from test to test depending on the test objectives. For some sites, in-stack series cyclones were attached to the sample probe inlet to remove large (greater than 10 µm) and coarse (2.5 to 10 µm) particulate fractions prior to dilution. Various numbers of sample collection media were selected depending on the species to be measured. The exact sampler configuration was established prior to the field campaign to ensure all sample media and components were available in the field. Run times were selected to optimize the amount of sample collected on each media. Typically, run times of six hours were selected for gas-fired sources to maximize the number of elements and organic compounds that could be detected within a reasonable test day. Shorter run times (e.g., 20 minutes for a Diesel engine) were conducted when high analyte concentrations were present.

Field Procedures

- Preliminary tests: A preliminary velocity and molecular oxygen (O_2) traverse was performed prior to sample collection to determine representative locations for the sample probes (single point sampling was used in all tests).

- Pre-test velocity traverse: Prior to each test, a full velocity traverse of the stack was performed with a Pitot tube/thermocouple assembly. The resulting velocity profiles were used with the single point velocity measurement during the test and post-test velocity traverses to determine the average stack gas flow rate during each test.

- Pre-sampling: The dilution sampler and ancillary components were raised to the sampling location, assembled, loaded with sample media and leak checked prior to sample collection. Special attention to handling of filter cassettes was taken to avoid overtightening of the filter cassettes and resultant damage to filters for gravimetric analysis (this was implemented after such problems were encountered in two tests). The leak check procedure involved plugging the sample inlet (excluding the sample probe and venturi, which were leak checked separately), closing the dilution air and bypass control valves, turning on the sample media bypass pump and adjusting it to maintain a slight vacuum (a few inches of water) similar to that typical of sample runs, then measuring the flow rate. A maximum leak rate of 2 percent of the total flow through the tunnel was considered acceptable. The data acquisition system was configured for site-specific parameters. A sample nozzle of appropriate diameter was selected and installed to approximate isokinetic sampling, although this was not considered a critical requirement. Just prior to sample collection, the probe and sample venturi where heaters were turned on and set to the target temperature (typically 150 to 175 °C).

- Sample collection: Prior to inserting the sample probe, the high volume bypass fan was turned on to start dilution airflow and flow through the sample probe. The high volume fan speed and position of the dilution airflow valve were set to achieve the target sample flow rate and dilution ratio for the test. Once conditions were set, the probe was inserted into the stack to the appropriate sampling point, and final adjustments to flows and temperatures made. Once the target sample flow rate (typically 25 liters per minute (L/min)) and dilution air flow rates (typically 500 to 1000 L/min, depending on target dilution ratio) were achieved, the sample collection media pumps were turned on to commence the sampling run. The exact time that sampling commenced was noted to facilitate sample volume calculations. Sample media flow rates were adjusted to the target rates, and then final adjustments to the high volume fan speed and dilution airflow valve were made to reach the target sample flow rate and dilution ratio. The data acquisition system displayed a real-time indication of the actual dilution ratio. During the test, select data was manually logged at 15-minute intervals as backup and supplement to the data acquisition system data. All flow rates were monitored and adjusted if needed to maintain target flow rates. At the completion of the target run time, the sample media pumps were turned off and the exact time was noted. The probe was removed from the

stack, the heaters were turned off, and the heated components allowed to cool before handling.

- Sample Recovery: Sample recovery consisted of two main parts: (1) removing and isolating the sample media prior to storage at low temperature; and (2) quantitatively rinsing the probe and sample venturi to recover any deposits. Removing and isolating the sample media was a relatively straightforward operation consisting of unplugging the filter packs and other media and sealing the inlets and outlets with caps. These were then removed to on-site storage (refrigerated where necessary) prior to shipment to the laboratory. The probe and sample venturi were rinsed with DI water and acetone, or with acetone alone, following EPA Method 5 (U.S. EPA, 1996a) procedures.

- Sample Custody and Shipping: Conventional procedures were used to pack and ship samples to the laboratory for analysis. Specific procedures are outlined in standard operating procedures for ambient air samples; hence, these are not described here.

Post-Test Procedures:

- Sample Analysis: Sample analysis procedures are described in detail in the site-specific test reports. In general, analysis procedures followed ambient air sample analysis protocols; hence, these are not described here. PM mass in acetone rinses was determined using EPA Method 5 (U.S. EPA, 1996a) gravimetric procedures.

Further information on test procedures can be found in the test reports referenced in Section 1. The detailed procedures evolved over the course of the project and modifications were made as problems encountered and solutions improvised or developed. Further optimization of the field procedures is still needed to reduce errors and enhance quality assurance/quality control information. This effort is continuing with the development of a voluntary consensus standard under ASTM International.

DESIGN ASSESSMENT EXPERIMENTS

One factor in common with all of the recent applications of the Hildemann sampler is the relatively large physical size and weight of the sampler. Lee et al. (2000) noted that for portability the sampler needed to be constructed in several modular sections so that they could be lifted to the relatively confined spaces on elevated stack platforms to access the sampling location. Wien et al. (2003) noted that in one application, the DRI dilution sampler, plus all the ancillary sampling equipment needed for broad chemical speciation totaled approximately 500

kilograms (kg) including personnel, which was near the structural weight limit for the stack platform. Although this was an extreme case and the quantity of equipment and personnel would be a fraction of this for measurement of PM2.5 mass only, it highlighted the need for a more compact dilution sampler to broaden the applicability of the method. The original Hildemann design criteria were based on sound experimental results for laboratory generated aerosols over a limited range of conditions and a limited series of field experiments on actual combustion systems. To further refine design criteria for those parameters most affecting the size and weight of the sampler, a series of experiments was conducted using the DRI sampler for a range of flue gas compositions generated using a pilot-scale laboratory combustor.

The overall goal of the pilot-scale evaluation was to experimentally understand and quantify design criteria for a more compact and easier-to-use dilution sampler that preserves comparability of PM2.5 mass results to the Hildemann design. In addition, supplementary tests and engineering analysis were undertaken to understand the characteristics of the current dilution tunnel performance to aid in interpreting pilot-scale test results. The specific objectives of these tests were:

- Quantify PM2.5 mass and ultrafine particle number size distributions via dilution sampling from the pilot-scale combustor with natural gas, residual oil and coal;
- Determine effect of residence time and dilution ratio on PM2.5 mass and ultrafine particle number distributions over the range of 10:1 to 50:1 dilution and 2 to 80 seconds residence time;
- Determine the minimum residence time and dilution ratio for stable mass and size distributions for different exhaust conditions and matrices.
- Determine the effect of exhaust gas temperature on PM2.5 mass.
- Evaluate particle losses in the dilution sampler over a range of solid and condensable particle concentrations.

The results of the tests are described in detail elsewhere (Chang and England, 2004b). The main findings of the tests were:

- Scanning mobility particle sizer (SMPS) and chemical speciation results at different residence times in the dilution sampler suggest that an aging time after dilution of approximately 10 seconds or slightly more is adequate for vapor condensation growth and particle agglomeration. Shorter residence times may be adequate for sampling sources with high aerosol and/or condensable vapor concentrations.

- A minimum dilution ratio of 20:1 is necessary to obtain stable particle size distributions. The total mass of PM2.5 was not affected by dilution ratio.

- Particles 0.1 μm in aerodynamic diameter and smaller rapidly accumulate into larger particles (typically in less than 10 seconds).

- Deposits of particles in the undiluted portions of the sampling system (i.e., sample nozzle, sample probe, venturi, etc.) can be significant and should be recovered for each sample run. Further development of recovery procedures for these components is needed to reduce imprecision and improve accuracy.

COMPACT SAMPLER DESIGN

Based on the pilot-scale test results, a compact dilution sampler was designed, constructed and tested. Figure 2-9 shows a schematic arrangement of the compact sampler. The raw stack gas sample is continuously extracted through a probe inserted into the stack and transported to the dilution sampler mixing section, where the sample is mixed with filtered ambient air to cool and dilute the sample. For most tests during this program, the entrance to the probe was fitted with in-stack cyclones to remove particles larger than 2.5 μm, so that all deposits recovered from the probe and sample venturi may be attributed approximately to PM2.5. The sample is diluted with ambient air that has been passed through HEPA and activated carbon filters. The diluted sample then enters an aging section with a bulk mean gas residence time of approximately 10 seconds. Excess diluted sample is bypassed through slots located in the wall of the sampler between the mixing and aging sections. A high-volume blower with a variable speed motor located in the bypass stream induces the flow through the sample probe and dilution air filter system. The speed of the bypass fan and the position of a slide gate valve located on the dilution air inlet are adjusted to achieve the target raw sample and dilution air flow rates. A PM2.5 cyclone (Bendix Model 240-type; Chan and Lippmann, 1977) is positioned inside the exit end of the aging section, through which the diluted and aged sample is withdrawn for collection on various media. Sample flow through the various media is induced using vane-type vacuum pumps, and some of

the flow may be bypassed to maintain the design total flow rate through the aging section and PM2.5 cyclone. The sampler is fitted with various temperature, pressure and relative humidity sensors needed to control sampler operation and document sample conditions.

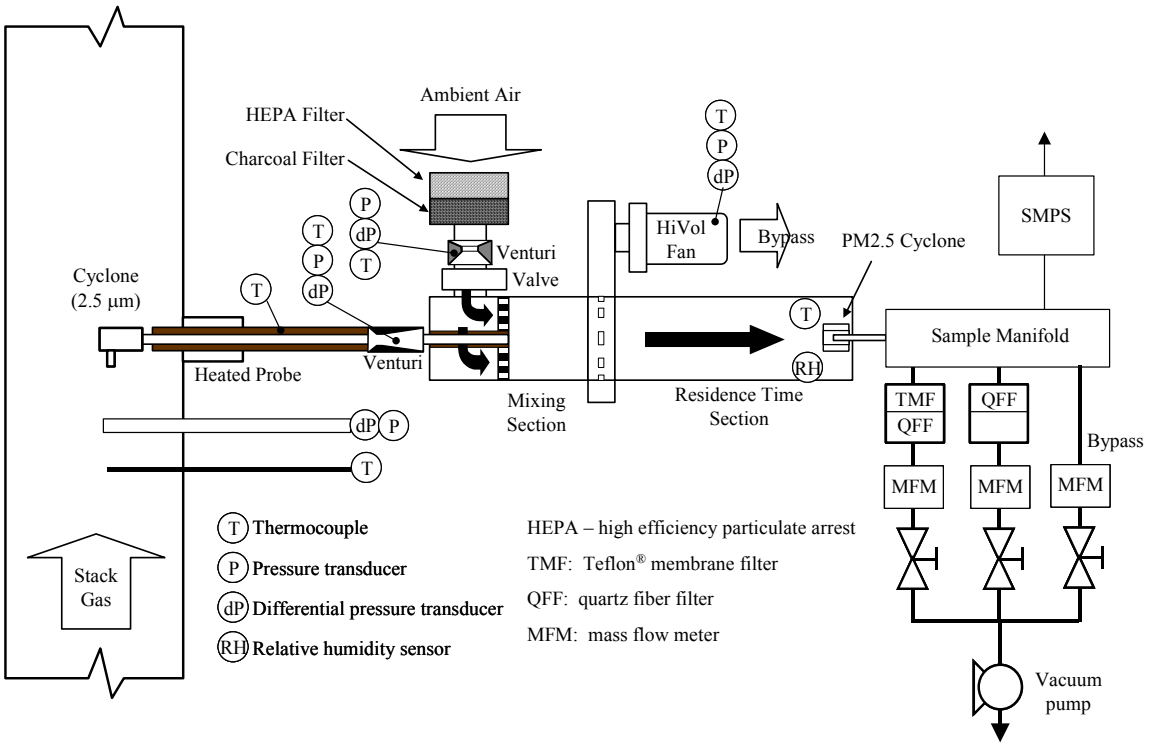


Figure 2-9. Compact Dilution Sampler.

The key design differences compared to the DRI sampler are:

- The heated sample transfer line between the probe and venturi was removed providing a direct connection[1];
- The mixing section was shortened by adding a mixing plate to produce more rapid mixing between the dilution air and the sample gas;
- The physical size of the residence time chamber was reduced by reducing bulk mean gas residence time from approximately 80 to 10 seconds and sample flow rate through the aging section from 226 to 113 L/min at nominal design conditions; and

[1] The flexible line was eliminated to minimize potential particle deposits prior to the dilution chamber. The compact sampler is small enough that a flexible connection should not be needed in most routine stack sampling locations.

- The sample path through the probe and dilution sampler is linear rather than convoluted to minimize inertial particle losses in the system and facilitate traversing from conventional stack monorails.

- The total flow rate through the aging section was designed for a flow rate of 113 L/min rather than 226 L/min. This provides sufficient sample volume for determination of PM2.5 mass, ions, elements, and organic carbon/elemental carbon (OC/EC). An extension to the aging section was designed to allow double the flow rate while maintaining the same residence time, when additional speciation measurements are desired.

Key design specifications of the DRI and the compact samplers are compared in Table 2-2. The sampler was designed for a nominal raw sample flow rate of 25 L/min, dilution ratio of 20:1, aging time of 10 seconds, and diluted sample flow rate of 113 L/min. The sample is introduced to the mixing section through a tube along the axis of the dilution sampler, and mixing is accomplished by introducing the dilution air through an array of parallel jets surrounding the sample jet. The goal of the mixing design is to fully mix the sample and dilution air within a short distance (1.4 sampler diameters), while avoiding back mixing and minimizing deposition in the sampler, with relatively low pressure drop. The design includes a PM2.5 cyclone (Bendix Model 240-type) after the aging section, similar to the approach used by Hildemann and others; however, this may be removed, depending on specific test objectives. In the present program, the diluted sample was conveyed to a sample manifold and distributed to the various sample collection media as shown in the figure.

All surfaces in contact with the sample are Type 316 stainless steel, which is reasonably inert chemically, electrically conductive, and easy to clean and recover any deposits from. The original Hildemann design and its DRI derivative do not employ any surface coatings. Teflon® coating of internal surfaces was considered to improve resistance to corrosion, but was rejected in favor of minimizing electrostatic particle losses by maintaining electrically conductive surfaces throughout the system. While Type 316 stainless steel is vulnerable to corrosion from acids in the sample if the acid concentration is high enough and corrosion could contaminate the samples, the potential impact of electrostatic losses on data quality was considered to be of greater significance in this program.

Table 2-2. Design Specification Comparison for DRI and Compact Dilution Samplers.

Design Parameter	Units	DRI Design	Compact Design
Raw Sample Flow Rate	L/min	25	25
Dilution ratio (nominal)	--	40	20
Dilution air flow rate (nominal)	L/min	1000	500
Dilution ratio (range)	--	25-50	10-40
Dilution air flow rate (range)	L/min	625-1250	250-1000
Mixing Section diameter	cm	15	20
Effective mixing length	diameters	18	1.4
Mixing section type	--	1-step, single cross-jet	1-step, multiple parallel jets
Mixing section Reynolds number (nominal)	--	9000	6000
Aging section diameter	cm	46	20
Aging Section Flow Rate (nominal)	L/min	226	113
Aging section length (nominal)	cm	183	60
Aging section residence time (nominal)	sec	80	10
Aging section Reynolds number (nominal)	--	1000	800
Aging Section Flow Rate (extended)	L/min	n/a	226
Aging section length (extended)	cm	n/a	120
Aging section residence time (extended)	sec	n/a	10
Aging section Reynolds number (extended)	--	n/a	1500
Bypass (nominal)	L/min	799	412
Bypass (range)	L/min	424-1049	49-912
Overall Length* (approximate)	cm	90	135
Overall Width* (approximate)	cm	60	25
Overall Height* (approximate)	cm	200	45
Overall Weight* (approximate)	kg	120	20
Dilution Air Conditioning**	--	HEPA + activated charcoal	HEPA + activated charcoal
PM2.5 cyclone after aging	--	Yes	Yes
Materials (sample side)	--	Stainless steel	Stainless steel
Sample Flowmeter	--	Venturi	Venturi

*Dilution sampler only; ancillary equipment for sampling media not included.
**Use optional dilution air dehumidifier if needed to maintain sample below 70% relative humidity.

Dilution Sampler Size and Portability

User friendliness of dilution sampling equipment is a necessary ultimate objective for routine and widespread use of the method. Therefore, one of the goals was to design a sampler that is approximately comparable in size and weight to traditional particulate sampling equipment. The compact dilution sampler is constructed in modular sections of less than 9 kg weight each, connected by V-band clamps, to facilitate hauling to elevated stack platforms and easy cleaning. A traditional EPA Method 5 (U.S. EPA, 1996a) sampling train, loaded with sample collection media and charged with ice, including sample pump and control module, typically weighs in the range of 20 kg. The physical size and weight of the compact dilution sampler is approximately similar to a standard Method 5 sampling train (Figure 2-10). The compact dilution sampler is designed in four main modules plus pumps and control console, which is comparable in

complexity to the Method 5 train. For determining PM2.5 mass, only a single filter pack is needed and the amount of ancillary equipment is minimized (one pump, flow control valve and flow meter). Additional sample and sorbent packs require additional sample housings, pumps, and flow controls, adding somewhat to the size and complexity of the setup. The dilution sampler setup required to speciate PM2.5 mass for elements, ions, OC, EC, and semivolatile organic compounds (SVOC). The SVOC component is by far the largest, and would not be used in most routine test programs) is somewhat larger than the EPA Method 0020 Source Assessment Sampling System (SASS; U.S. EPA, 1986). Thus, the compact dilution sampler offers similar complexity and size for measuring PM mass, while also offering the capability for expanded PM chemical speciation and size measurements, that is roughly comparable in size and weight to traditional sampling equipment.

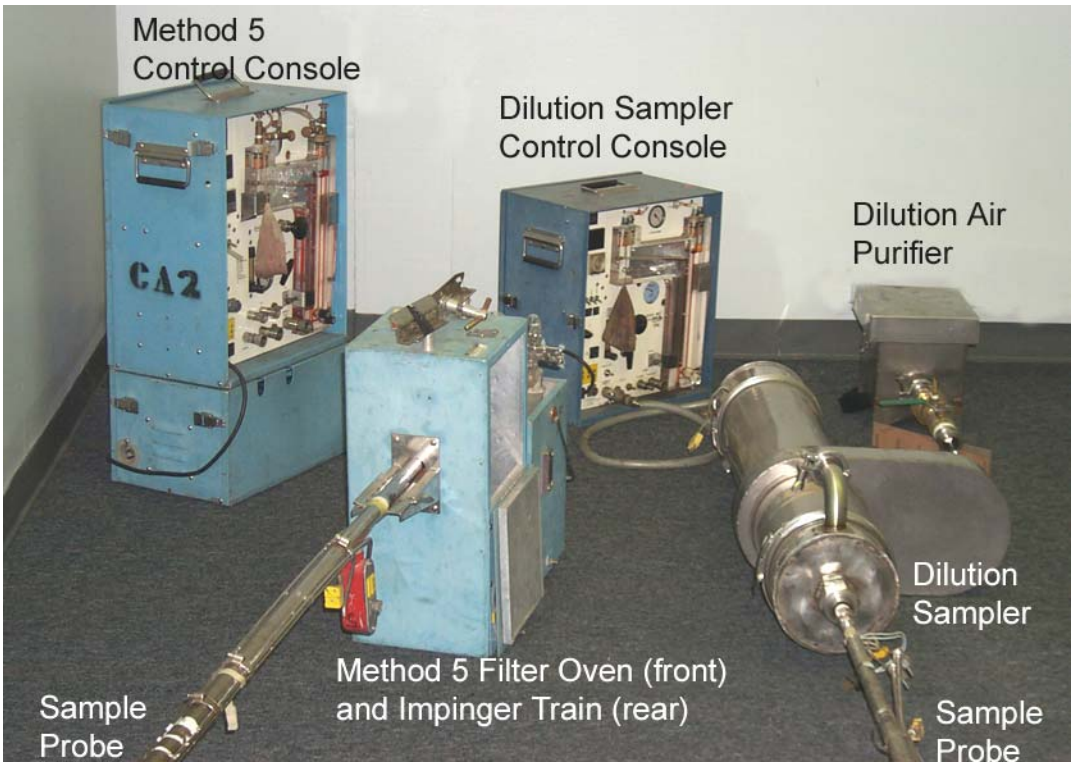


Figure 2-10. Size Comparison of Method 5 Train (left) and Compact Dilution Sampler (right).

Instrumentation and controls

The dilution sampler instrumentation consisted of thermocouples, flow elements (sample and dilution air venturis, orifice for bypass fan, thermal mass flow meters for sample media),

differential pressure transducers (for Pitot tube, venturi and orifice meters), and relative humidity elements (for dilution air and diluted sample). In some cases, rotameters and pressure gages were used. The outputs from the pressure transducers, thermocouples, relative humidity sensors and thermal mass flow meters were connected to a data acquisition system, consisting of data logger (Campbell Scientific) and a laptop computer. Conceptually, the data acquisition system is simple using off-the-shelf hardware and software. Although the system also was capable of controlling output to automate operation of the dilution sampler, this was not implemented in the current program. Automated operation of the sampler would significantly simplify the use of the sampler and improve precision of sampling conditions.

COMPACT SAMPLER AND DILUTION METHOD PERFORMANCE

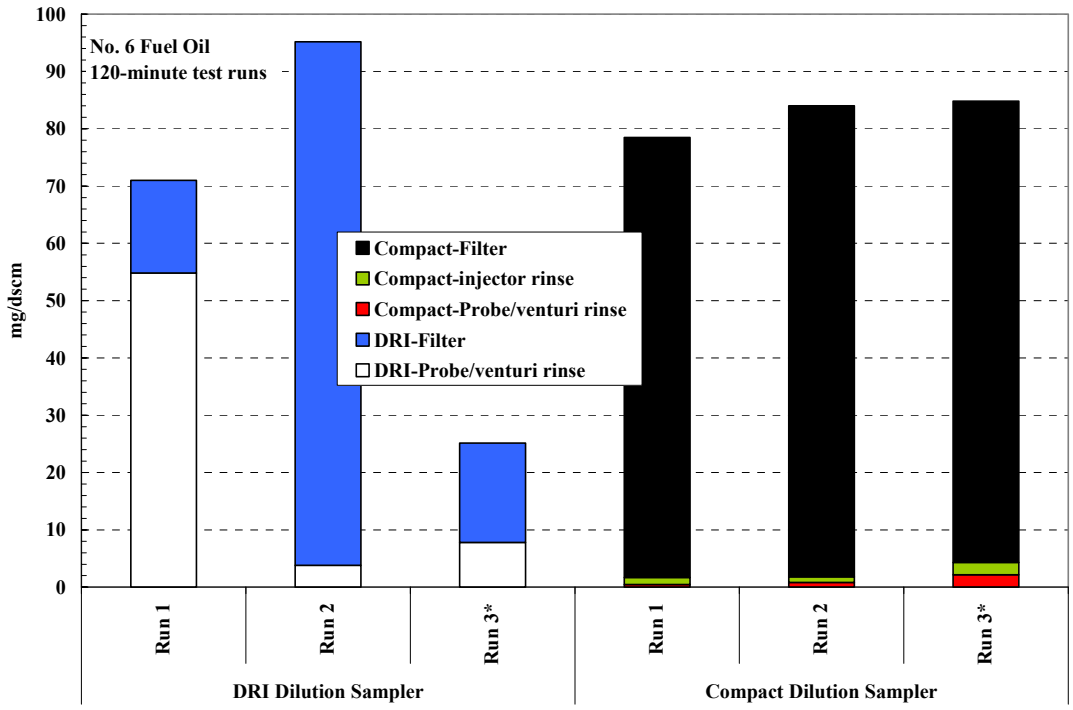
Mixing Performance (Radial Profiles And Cold Flow Characterization)

Mixing tests were performed to verify components of the sampler design. Radial and axial gas tracer concentration profiles were measured to verify completeness of mixing between the sample and dilution air prior to the bypass. Flow visualization tests were performed using smoke injection in an acrylic plastic mockup of the unit to evaluate the flow pattern within the mixing and aging areas. In addition, radial particle number concentration profiles were measured during combustion tests. While mixing completeness of better than 90 percent was verified prior to the bypass, the flow visualization tests revealed some areas of back mixing within the mixing and aging sections. This was considered acceptable for the initial design, since comparable back mixing was evident in the DRI dilution sampler aging section. Further details of these results are reported elsewhere (Chang and England, 2004b).

Pilot Combustor Tests

A limited series of tests were conducted on the pilot-scale furnace to develop a preliminary comparison between the DRI and compact dilution samplers. Concurrent PM2.5 mass measurements using the compact dilution sampler and the DRI dilution sampler were made while firing No. 6 fuel oil. Three 120-minute test runs were planned; however, Run 3 results are highly questionable because of abnormal combustion conditions (clogged fuel atomizer), and the run was terminated at 53 minutes. Excluding Run 3, average total PM2.5 concentration

measured by the compact dilution sampler (81 milligrams per dry standard cubic meter (mg/dscm)) and DRI dilution sampler (83 mg/dscm) are in good agreement. Deposits in the probe and sample venturi are somewhat higher in the DRI system, with Run 1 showing an abnormally high catch compared to earlier tests (Figure 2-11). Nevertheless, the results show that, for these conditions, the two dilution samplers are capable of giving approximately similar PM2.5 mass results. Similar tests with natural gas were abandoned because background levels due entrainment of furnace deposits were shown to be significant in earlier tests. Further details of the test results are reported elsewhere (Chang and England, 2004b).



*Run 3 invalid due to abnormal combustion, run terminated after 53 minutes.

Figure 2-11. PM2.5 Mass for Compact and DRI Dilution Samplers for No. 6 Fuel Oil Combustion in Pilot-Scale Furnace (Chang and England, 2004b).

Field Comparison Tests

Concurrent measurements with the compact and DRI dilution samplers were conducted at two field sites: a Diesel engine powered backup generator (Hernandez et al., 2004) and a natural gas-fired combined cycle power plant (England et al., 2004). Based on six concurrent test runs (three at 50 percent load and three at 75 percent load) on the Diesel engine, a slight positive bias

(average 1.3 percent) and slightly greater random variation were observed with the compact sampler compared to the DRI sampler (Figure 2-12). The differences are not significant at the 95 percent confidence level. Tests on the natural gas-fired combined cycle power plant showed similar comparability, at much lower PM2.5 concentrations (Figure 2-13). Due to high winds that interfered with measurements during high load Runs 1 to 3, results from these runs may not be reliable. Although a negative bias (–6 percent, based on the average of all results excluding high load Runs 1 through 3) in the compact sampler results is apparent, it is not significant at the 95 percent confidence level due to the variability of the results. These results include only the dilution sampler filter results since the probe and venturi acetone rinse results for these tests are indistinguishable from the acetone blank. Based on results shown earlier in Figure 2-4, these deposits are probably less than 5 percent of the total mass assuming all particles are smaller than 1 µm. As noted later in this section, the absolute PM2.5 concentrations shown in Figure 2-13 are probably biased high due to background levels in the dilution air, but the bias is similar in magnitude for both samplers.

These results provide a preliminary indication that the compact sampler and DRI sampler are capable of producing similar results, within the confidence bounds and under the conditions evaluated in this program. Due to the limited number of tests, the confidence bounds around the mean result for each series of tests is relatively large, and any bias in the compact sampler results smaller that this cannot be discerned with high confidence. Further tests are needed to better quantify method performance (systematic and random variation), especially for applications with extremely low PM concentrations (less than approximately 1 to 2 mg/dscm).

Measurement Background – PM2.5

PM2.5 field blanks were generally not significant. However, dilution system blanks (DSBs) at Sites Charlie (a gas-fired refinery process heater) and Echo (a natural gas-fired combined cycle

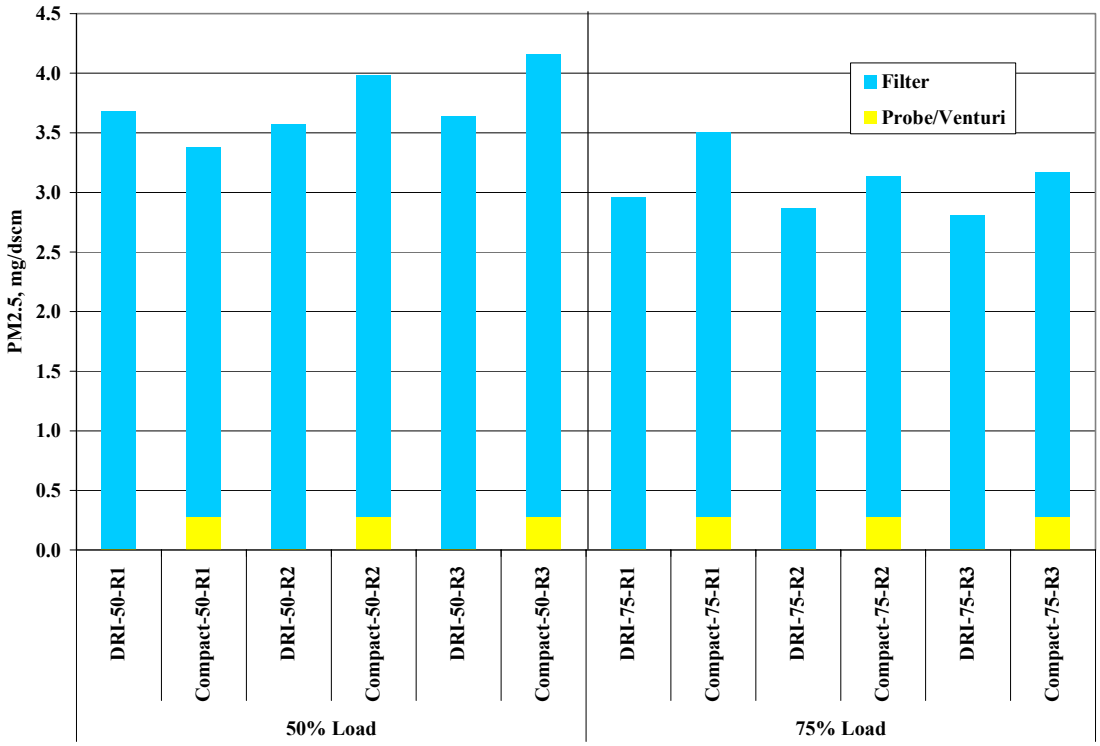


Figure 2-12. Comparison of DRI and Compact Dilution Sampler PM2.5 Results for a Diesel Engine with Diesel Particulate Filter (Hernandez et al., 2004).

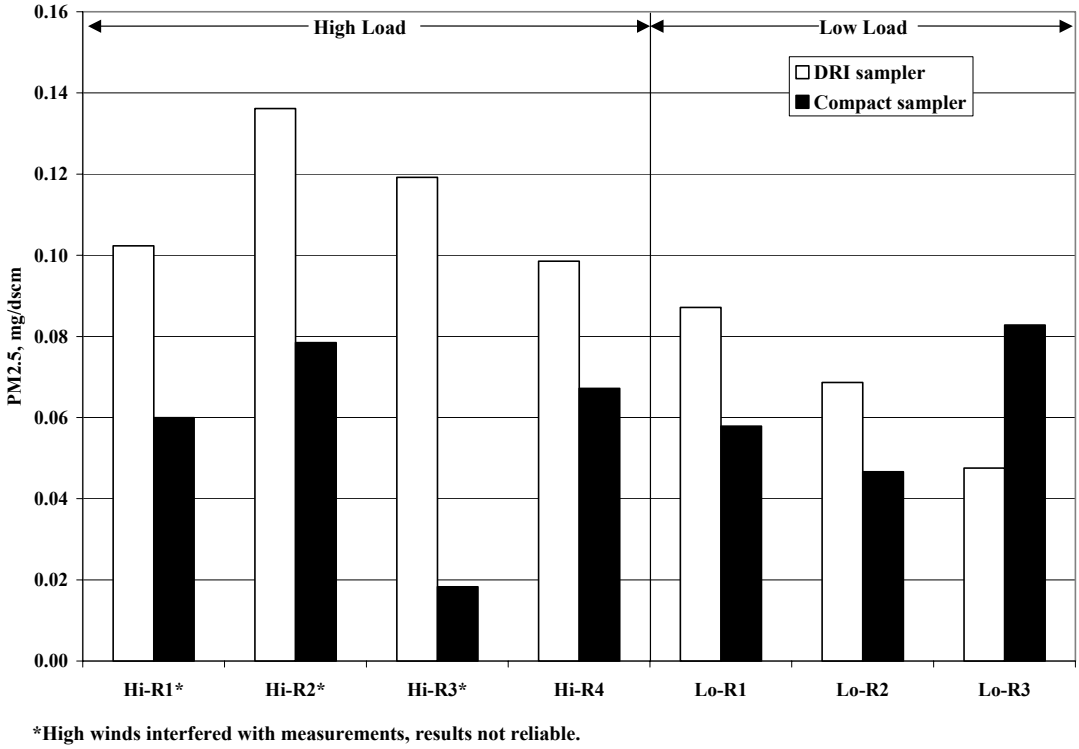


Figure 2-13. Comparison of DRI and Compact Dilution Sampler PM2.5 Results for a Natural Gas-Fired Combined Cycle Power Plant with Oxidation Catalyst and SCR (England et al., 2004).

power plant) indicated that background PM2.5 in the purified dilution air may be significant relative to the stack PM2.5 for sources with extremely low stack PM2.5 concentrations. This is more a consequence of the nature of the clean sources tested than of inherent limitations in the method. The DSBs were more significant than field blanks or trip blanks at the sites, indicating the source of the background was not contamination of the sampling media. Hourly ambient PM2.5 data from a nearby ambient monitoring station (AMS) were obtained for all test periods at Site Echo. The average hourly AMS PM2.5 ranged from 0.007 to 0.020 mg/dscm during the tests. During a single six-hour ambient PM2.5 measurement run at Site Echo, the average hourly AMS PM2.5 (0.012 mg/dscm) and the measured ambient PM2.5 (0.014 mg/dscm) are in very good agreement (Figure 2-14).

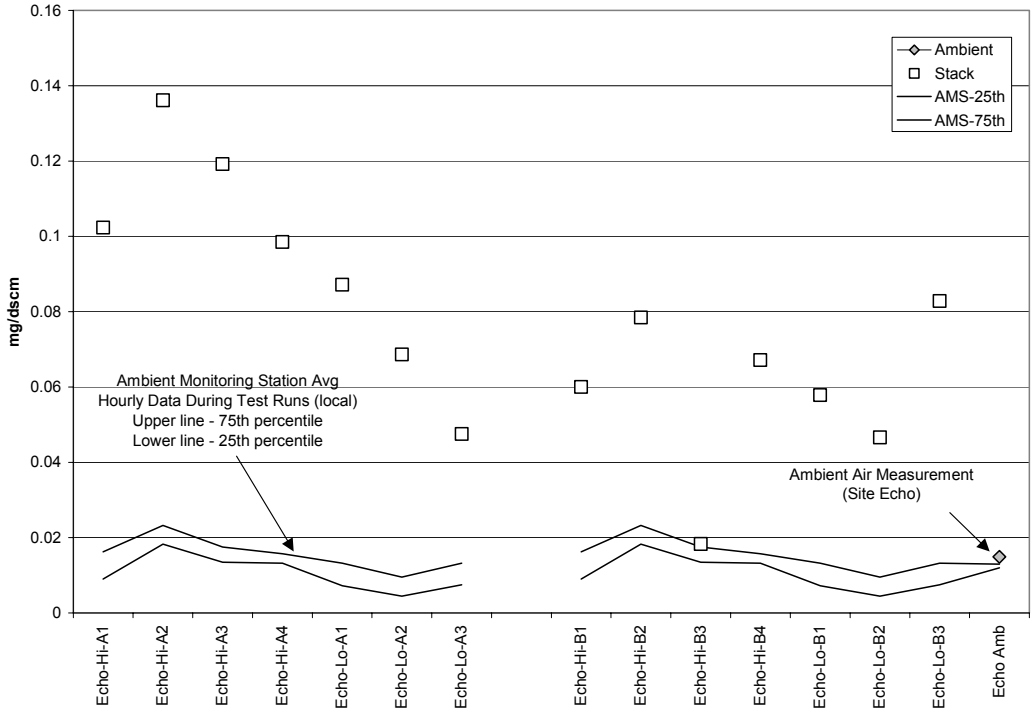


Figure 2-14. Stack PM2.5 and Ambient PM2.5 (Site Echo, England et al., 2004).

The AMS PM2.5 and the pre-test DSB results were used to calculate ambient PM2.5 penetration through the dilution air purifiers – i.e., the measurement background level in the dilution air – for each test run. Similar penetration efficiencies were calculated for the DRI (16 percent) and compact (24 percent) dilution samplers. The penetration factor was applied to the AMS PM2.5 during each stack test run to estimate dilution air background PM2.5 for each test. With the

exception of one of the seven data points for each dilution sampler, there is a fairly strong correlation between the variations in estimated dilution air background and stack PM2.5, and the levels are very similar (Figure 2-15). The variation in estimated dilution air background PM2.5 is primarily due to variation in AMS PM2.5 rather than sampling conditions. This implies that the observed variations are in fact systematic rather than random; therefore, the stack results can be corrected for the dilution air background. Subtracting the estimated dilution air background PM2.5 from the measured stack PM2.5, it can be seen that the corrected stack PM2.5 is very near zero, and practically indistinguishable from the AMS PM2.5 (Figure 2-16).

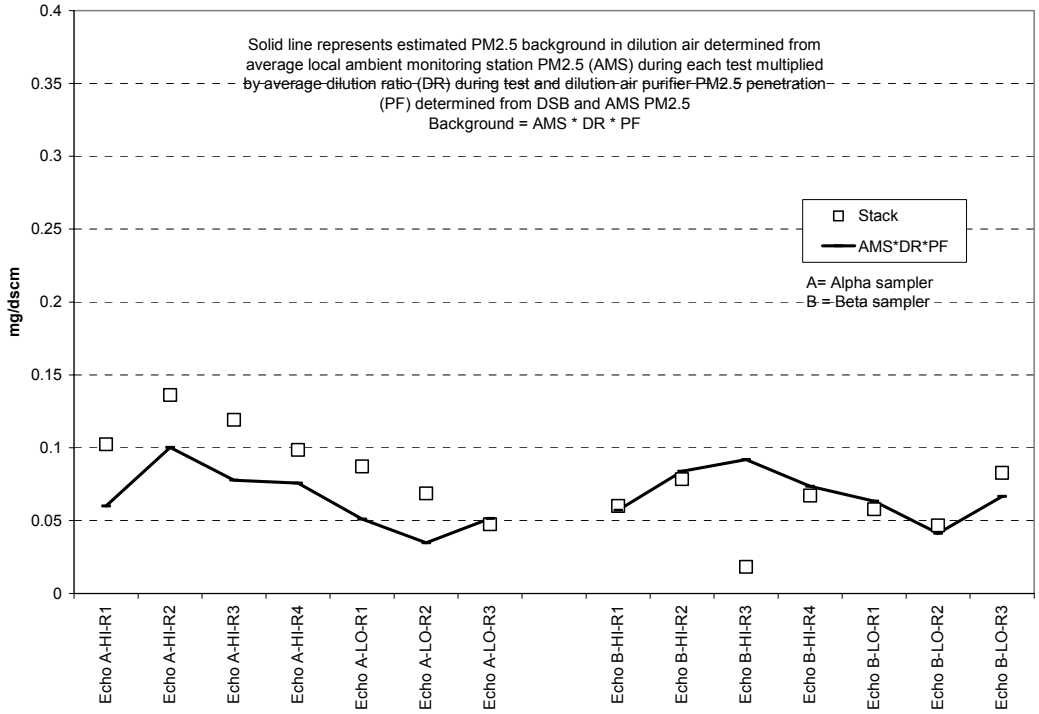


Figure 2-15. Stack PM2.5 and Estimated Dilution Air Background (Site Echo, England et al., 2004).

The pre-test DSB and stack results from Site Charlie are not quite as straightforward to interpret since AMS data are not available for the sampling periods (Figure 2-17). The single ambient PM2.5 measurement (0.041 mg/dscm) and single DSB, albeit not taken concurrently, suggest a PM2.5 penetration efficiency of only 5 percent during those tests. The single DSB for dilution air background PM2.5 at Site Charlie corresponds to an in-stack concentration of approximately

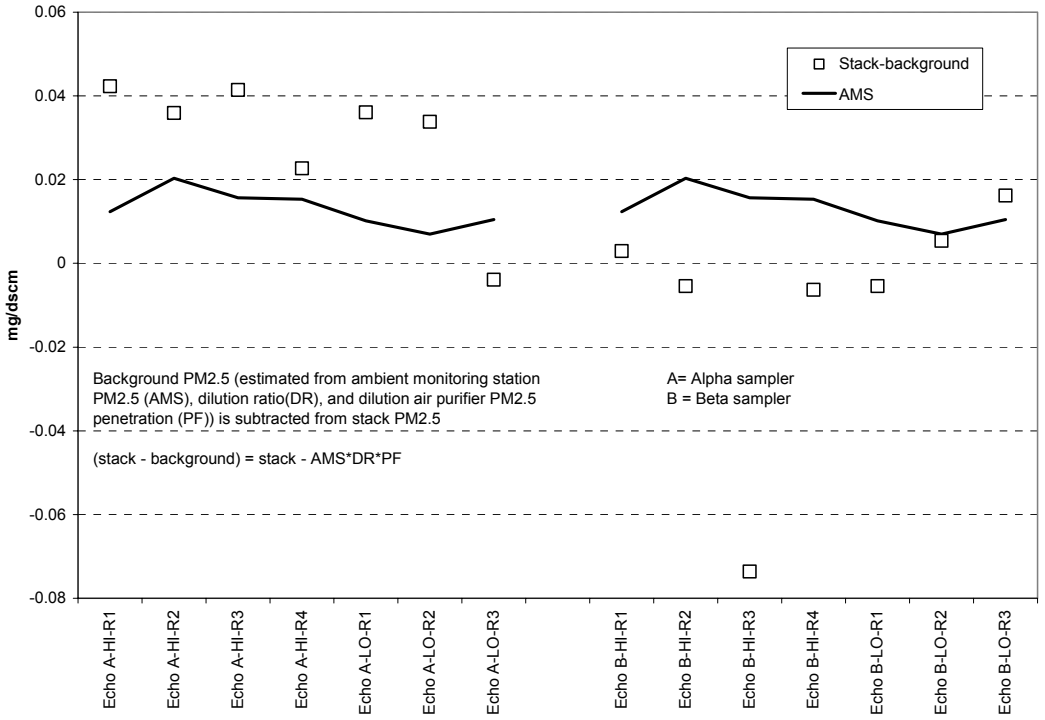


Figure 2-16. Corrected Stack PM2.5 and Ambient PM2.5 (Site Echo, England et al., 2004).

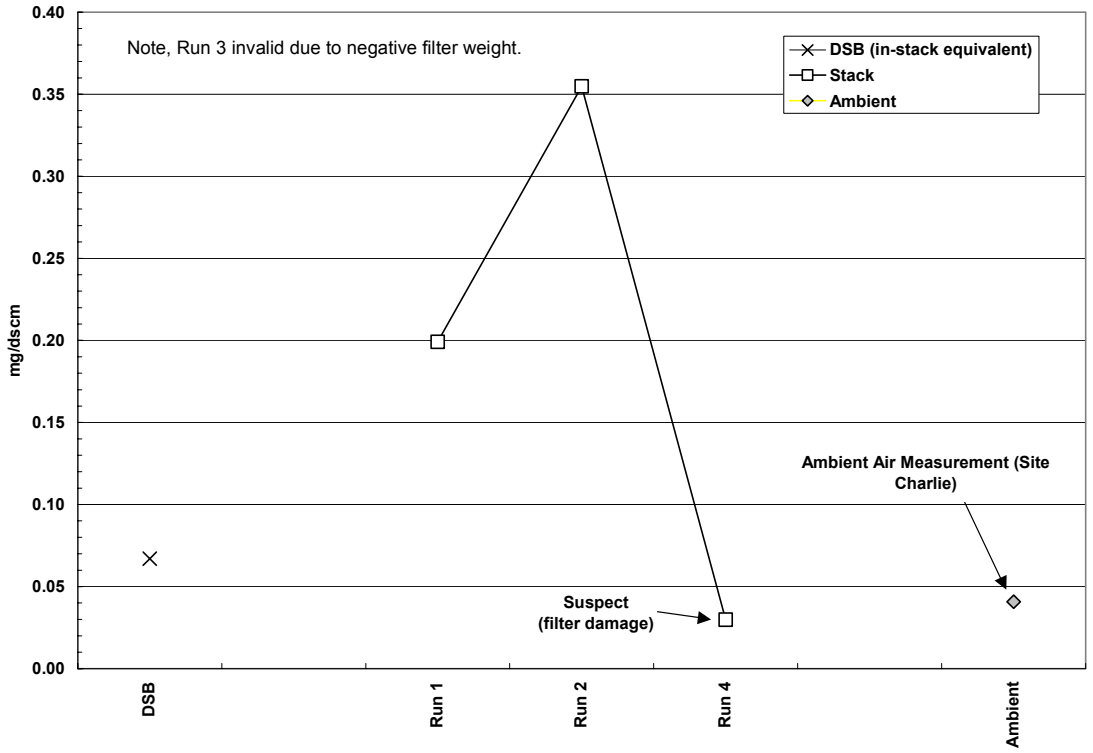


Figure 2-17. Comparison of Stack, Ambient and Dilution Air PM2.5 (Site Charlie, Wien et al., 2004b).

0.067 mg/dscm, or 35 percent of the average measured stack PM2.5 (0.19 mg/dscm). Because of the variability of the stack PM2.5 results, the 95 percent confidence lower bound of the mean stack PM2.5 is less than the DSB result, indicating the difference is not significant at that confidence level. The variability of the Site Charlie results is atypical due to a procedural error that damaged some of the filters.

Based on the significance of the dilution air background with the present sampling equipment, a DSB should be collected with every test, and ideally with every test run. It may also be possible to reduce the dilution air background levels by improvements to the dilution air filtration system. Therefore, until this issue is resolved, a modification to the dilution sampler design is recommended that would enable a filter cassette to be located in the purified dilution air supply between the filters and the dilution air venturi so that a DSB can be collected concurrently with each test run.

HEPA filters are typically rated for a minimum collection efficiency of 99.97 percent for particles 0.3 μm and larger. The DSB results from Site Echo imply an ambient air PM2.5 collection efficiency of approximately 76 to 84 percent across the dilution air HEPA and activated carbon filter assemblies in the compact and DRI samplers. Assuming the filters are performing to specifications, this suggests that the penetrating particles are smaller than 0.3 μm. This seems reasonable considering it is likely that the ambient air contains a significant fraction smaller than 0.3 μm. This suggests that reduced background levels could be achieved by improvements to the dilution air filter system. For example, ultra-low penetrating air (ULPA) filters, commonly used in clean rooms for pharmaceutical and semiconductor manufacturing facilities, have a rated for a collection efficiency of 99.9995 percent for particles of 0.12 μm and larger. This and other means of reducing PM2.5 background levels should be explored to reduce the systematic variation observed in these tests for applications with extremely low PM concentrations (less than approximately 1 to 2 mg/dscm).

PM2.5 Method Detection Limit (MDL) and Lower Quantification Limit (LQL)

The results from Sites Echo and Charlie suggest that background PM2.5 levels in the dilution air range from approximately 0.04 to 0.09 mg/dscm (10th to 90th percentile), depending on ambient

PM2.5. Although the variation in dilution air PM2.5 at Sites Echo and Charlie is more likely systematic rather than random and, therefore, not truly representative of measurement "noise," it can provide a conservative estimate of MDL and PQL. Using the DSB results from this test program, the estimated in-stack MDL (three times standard deviation) for the dilution sampler is approximately 0.051 mg/dscm and the in-stack LQL (ten times standard deviation) is approximately 0.17 mg/dscm based on the six-hour sampling periods used in these tests.

For this research program, six-hour test runs were selected to maximize the detection of individual PM2.5 species, especially organic compounds, which were expected to be present at much lower concentrations than total PM2.5 mass. However, six hours by no means represents a minimum requirement for determining PM2.5 mass only. The in-stack MDL or LQL will depend on many factors, including the sampling time chosen for the test. For integrated sampling methods, sample gas volume increases with sampling time for a constant sampling rate; therefore, assuming the analytical MDL (AMDL) is constant, the in-stack MDL decreases with increasing sampling time. Sampling time is typically selected prior to testing to achieve an in-stack MDL commensurate with the test objectives. Test run times for routine tests using traditional test methods typically range from 30 minutes to 4 hours, with 2 hours or less being the most common. The estimated LQL for a 1-hour dilution method test run ranges from 0.13 mg/dscm based on AMDL to 1.2 mg/dscm based on variation of PM in the dilution air background observed in these tests.

A comprehensive discussion of particulate sampling MDL and LQL for various sampling methods is beyond the scope of this report. Other studies have explored method precision, accuracy and quantification limits for traditional non-dilution particulate test methods (Arunkumar et al., 2004; Lanier and Hendrix, 2001; Rigo and Chandler, 1999; Shigehara, 1996; Brown, J.W., 1979; Hamil, et al., 1976). Data from these studies and the current project were used to compare in-stack LQLs for EPA Methods 5, 5I, 201A and 202, and the dilution methods (Figure 2-18). The populations of samples are generally small; for simplicity sake in this illustration, small sample bias was ignored; therefore, the estimated standard deviations and resultant LQLs are probably biased low by 10 to 20 percent.

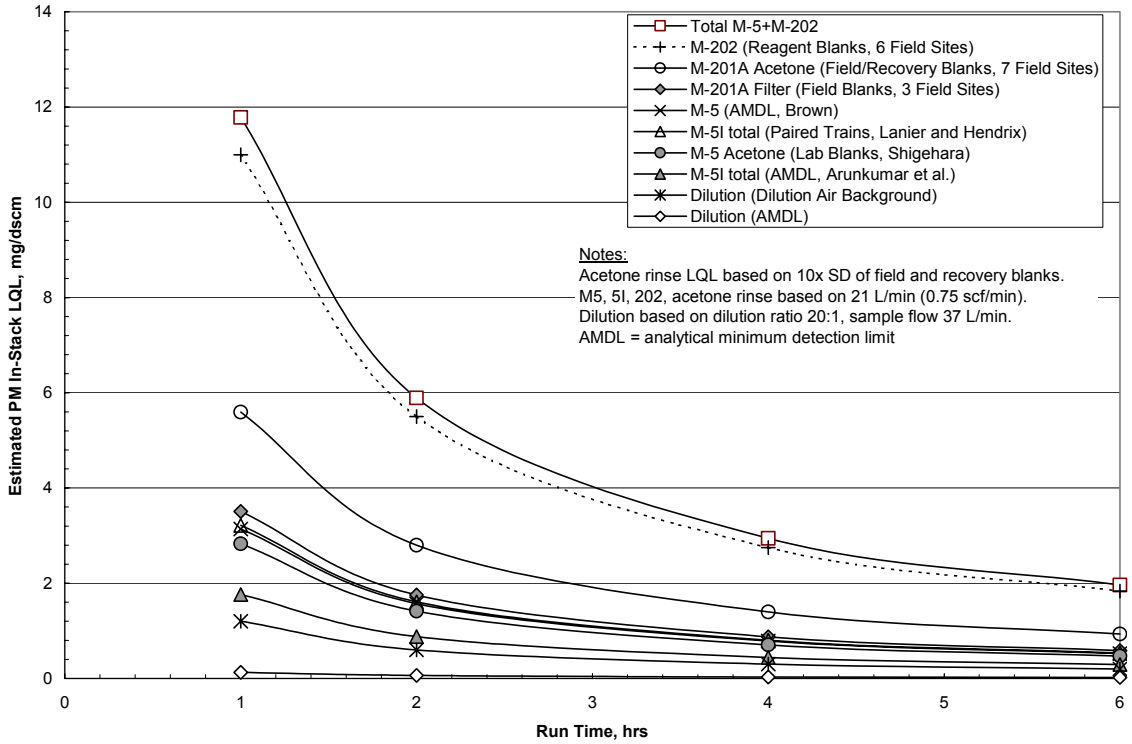


Figure 2-18. Comparison of In-Stack LQL as a Function of Sampling Run Time for Several PM Test Methods.

EPA Method 5 (which determines filterable PM using a heated out-of-stack filter; U.S. EPA, 1996a) results include the sum of a filter plus an acetone rinse of the sample nozzle, sample probe and front half of the filter housing. The filter is dried and weighed before and after testing to determine the mass of PM collected during the test. The acetone rinse is evaporated and dried in a tared beaker, and the net weight gain of the beaker represents the mass of particulate in the sample. The acetone rinse procedure is the same in EPA Method 5I (which determines filterable PM at low concentrations using a small integral filter and filter holder assembly; U.S. EPA, 1997a) and 201A (which determines filterable PM10 using an in-stack cyclone and filter assembly; U.S. EPA, 1996b), except that in Method 201A two acetone rinses are included for different sections of the cyclone/filter housing assembly (if determining both filterable PM10 and total filterable PM). EPA Conditional Test Method CTM-040 (U.S. EPA, 2002a; previously referred to as EPA Method PRE-004), which was used in this program, is a variation of Method 201A employing a second cyclone for determining filterable PM2.5 and incorporates a third acetone rinse. In this program, all of the acetone reagent blanks were well below the maximum

allowable residue limit specified in EPA Method 5 (not greater than 2.0 milligrams (mg)/250 milliliters (mL)).

Using the standard deviation of field sample train blanks and recovery blanks from the seven field sites tested in the current program and the prior API program, the LQL of the acetone rinse fraction alone is approximately 5.5 mg/dscm for a 1-hour sample run. Shigehara (1996) generated 22 sample train blanks in the laboratory, and based on these results the LQL of the acetone rinse procedure is approximately 2.8 mg/dscm for a 1-hour sample. The two different results appear reasonably consistent if one accepts it is likely that variability in the field would be greater than in the laboratory. Using the results of Brown (1979) and Arunkumar et al. (2004), the LQL based on AMDL for gravimetric analysis is in the range of 1.8 and 3.1 mg/dscm for 1-hour test runs, respectively. Using the results of Lanier and Hendrix (2001), the total LQL for Method 5I is estimated to be 3.2 mg/dscm with 1-hour test runs. Based on the most recent studies, it seems most likely that the LQL for filterable PM in a 1-hour test using traditional methods would be in the range of 2.8 to 5.5 mg/dscm.

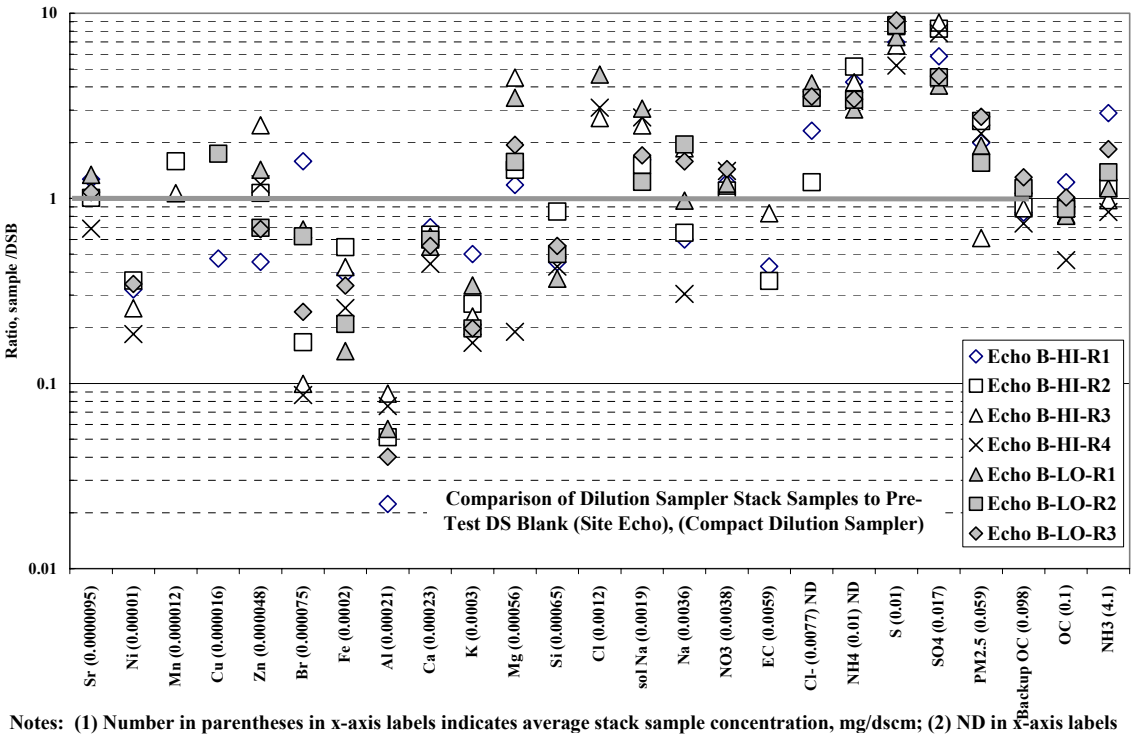
EPA Method 202 (U.S. EPA, 1996c) is used to determine condensable PM by bubbling a pre-filtered gas sample through a series of impingers partially filled with water and placed in an ice bath. The impinger solutions are then evaporated and dried to determine the net residue weight. The method includes a number of blanks (DI water, dichloromethane and a filter) used to correct the test results. Combining (by addition in quadrature) the standard deviations of the water, dichloromethane and filter reagent blanks taken over the course of the current program and the prior API program from six different field sites, the LQL for Method 202 is approximately 11 mg/dscm for a 1-hour sample run. Combining the filter results of Brown (1976), the acetone rinse results of Shigehara (1996) and the Method 202 results from this program, the estimated LQL for total particulate matter (filterable plus condensable) is approximately 11.8 mg/dscm. For total PM including condensable PM, the LQL is clearly driven by the LQL of the condensable test method, EPA Method 202.

The in-stack MDL for dilution sampling equipment and procedures used in this test program is significantly lower than the MDL for any of the traditional methods for filterable PM alone and far lower than the combined MDL for filterable and condensable PM. Based on AMDL, a

sampling time of 24 hours would be needed using EPA Method 5 to match the MDL for a 1-hour dilution sampling run (stated another way, the same MDL as a 1-hour Method 5 test theoretically could be achieved with dilution sampling in 2.5 minutes). However, as pointed out earlier, AMDL can be a misleading indicator of overall method MDL. More conservatively using the background variation in the dilution air as the basis for MDL, the same MDL as a 1-hour Method 5I test could be achieved with dilution sampling in 22 minutes. The dilution method measures both filterable and condensable PM, consistent with EPA's definition of primary PM (U.S. EPA, 2003b), together on the same filter. One would need to sample for approximately 12 hours using Methods 5I and Method 202 to match the LQL of a 1-hour dilution sampling run. Thus, the dilution method offers a very significantly improved in-stack LQL, for both filterable PM alone and the total of filterable plus condensable PM, compared to traditional stack test methods.

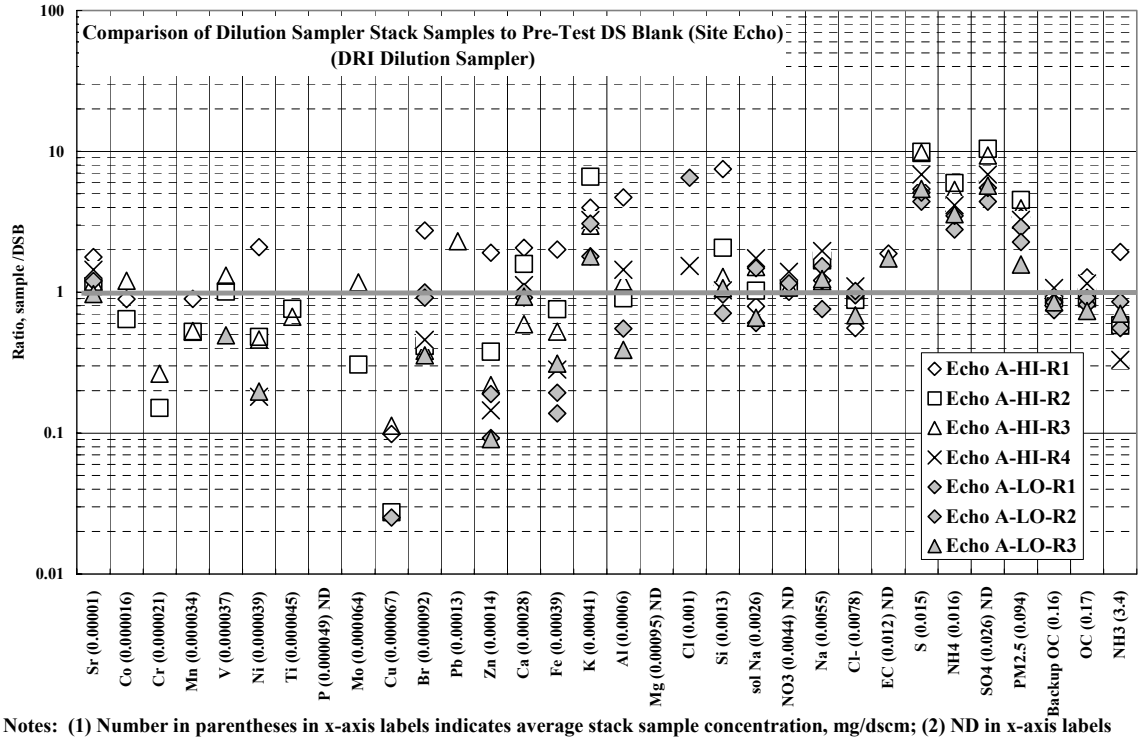
Measurement Background – PM2.5 Species and Precursors

Quality assurance blanks (field blanks, trip blanks, DSBs) indicated trace background levels of many substances within all categories of PM2.5 species (elements, ions, SVOCs) and volatile organic compounds (VOC). While field blanks and trip blanks were occasionally significant, the most significant levels were found in the DSBs collected at Sites Charlie and Echo. The DSBs provided an indication of background levels in all aspects of the sample including the dilution air. Since the field blanks and trip blanks were only occasionally significant, the results indicate that the dilution air is the most significant source of measurement background. Background levels indicate similar dilution air filter collection efficiencies across the DRI and compact dilution sampler filters, which is consistent with the common dilution air filter design. Although very low, the background levels are in many cases significant relative to the in-stack levels for gas-fired sources. To illustrate, Figures 2-19 to 2-23 present the ratio of stack results to DSB results for Site Echo. Results that have a ratio less than 1.0 indicate the background level was greater than the stack level; such results clearly are unreliable.



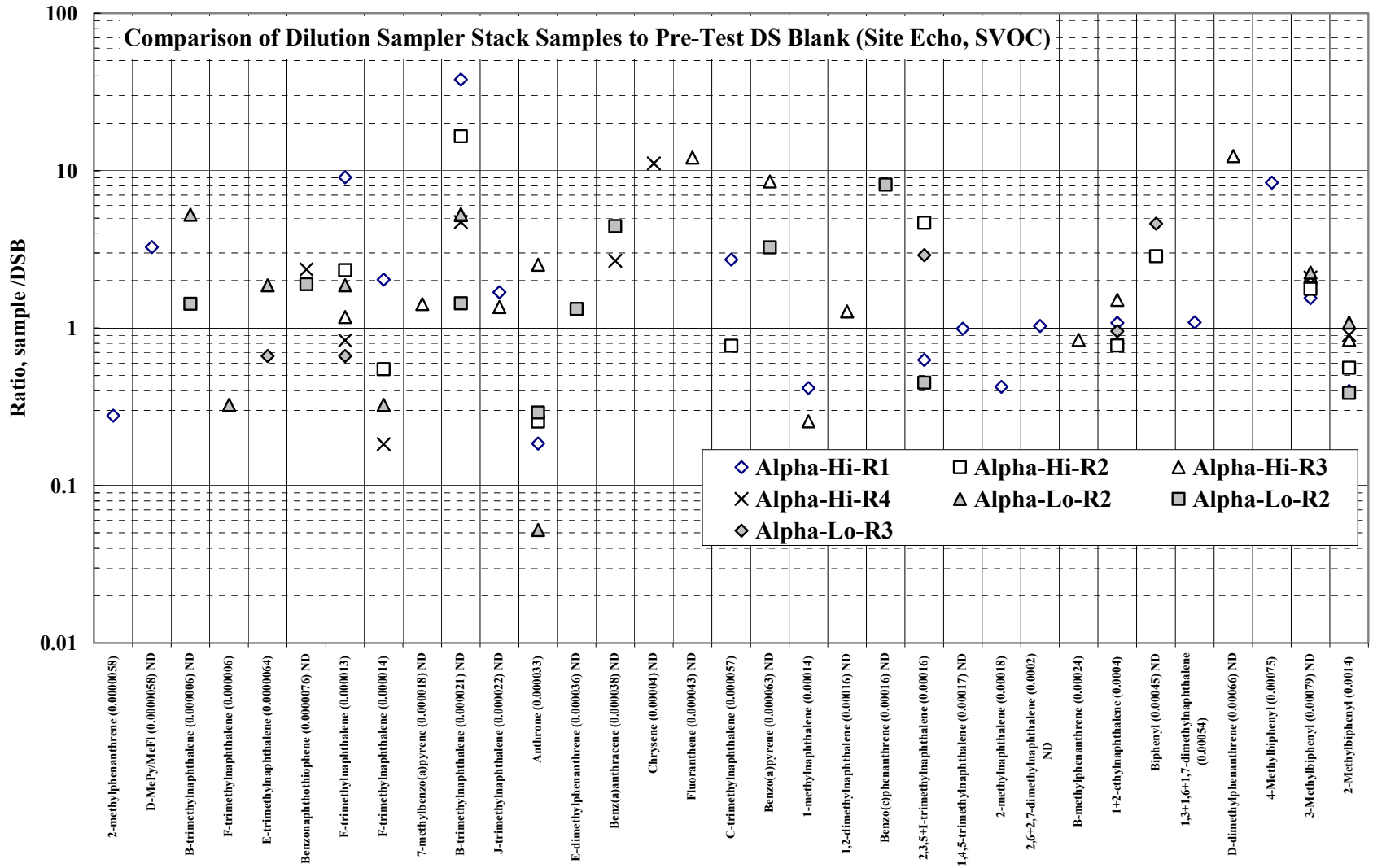
Notes: (1) Number in parentheses in x-axis labels indicates average stack sample concentration, mg/dscm; (2) ND in x-axis labels indicates substance not detected in blank, detection limit used for ratio.

Figure 2-19. Comparison of Stack and Pre-Test Dilution System Blank Results for PM2.5 Species (Compact Sampler, Site Echo).



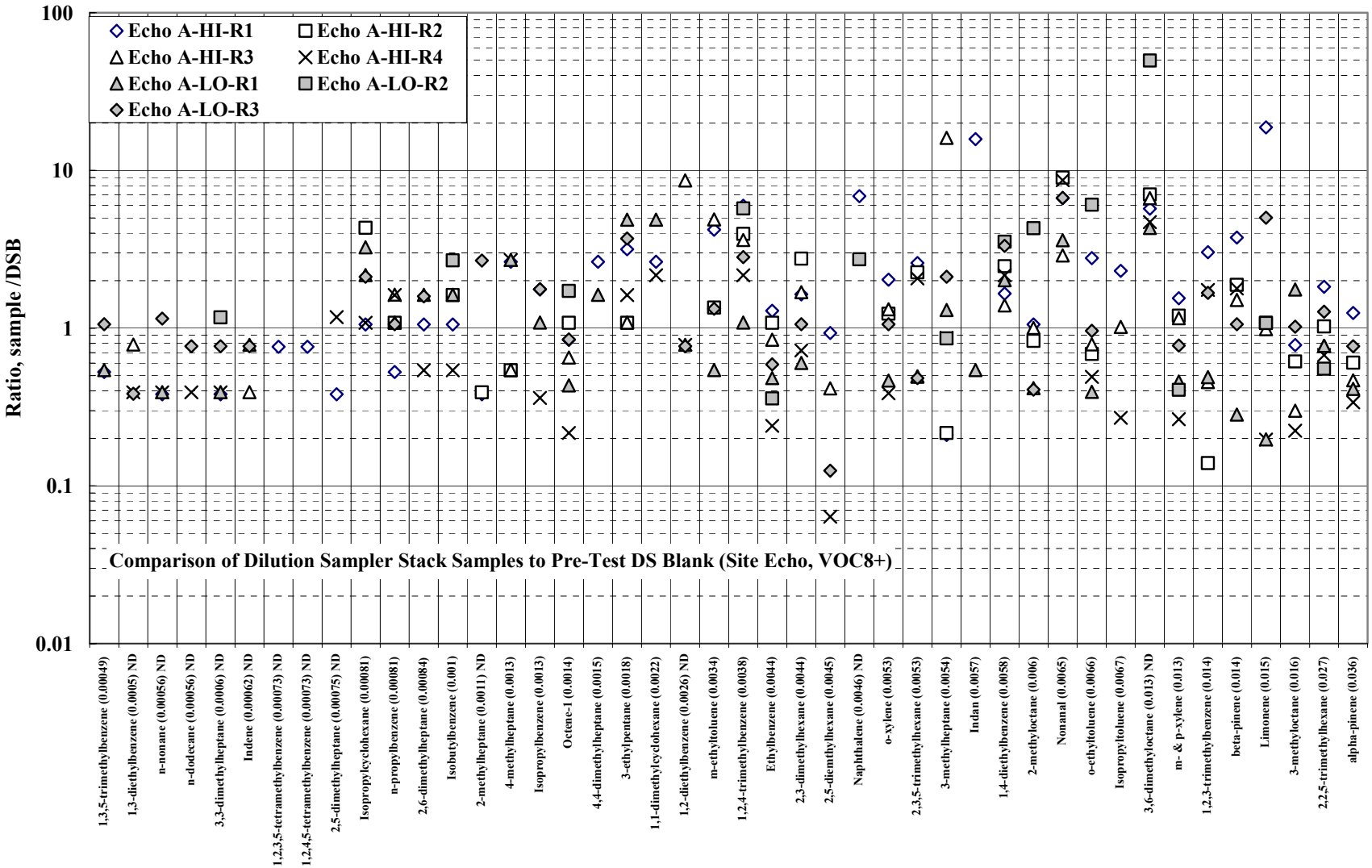
Notes: (1) Number in parentheses in x-axis labels indicates average stack sample concentration, mg/dscm; (2) ND in x-axis labels indicates substance not detected in blank, detection limit used for ratio.

Figure 2-20. Comparison of Stack and Pre-Test Dilution System Blank Results for PM2.5 Species (DRI Sampler, Site Echo).



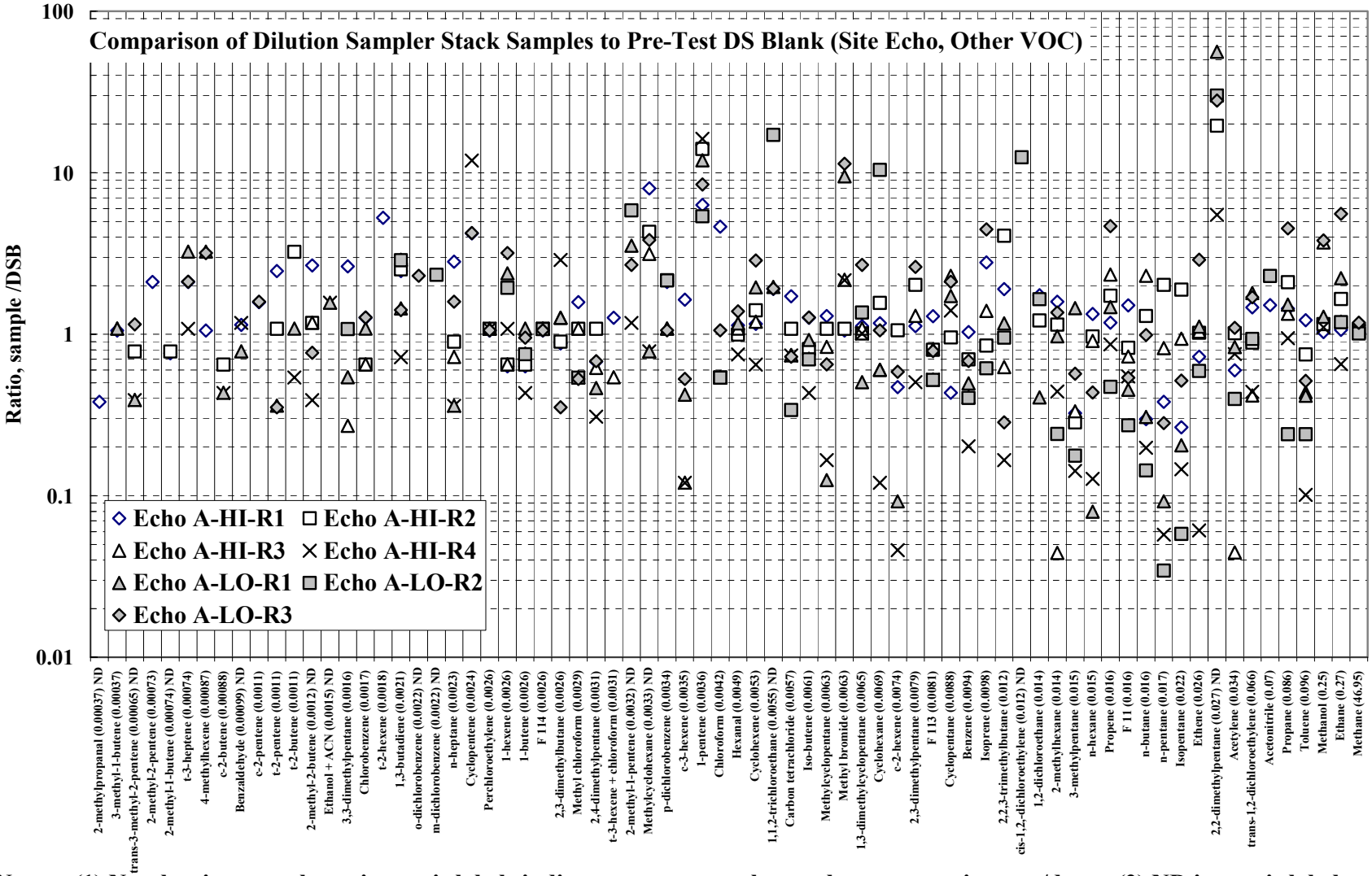
Notes: (1) Number in parentheses in x-axis labels indicates average stack sample concentration, mg/dscm; (2) ND in x-axis labels indicates substance not detected in blank, detection limit used for ratio.

Figure 2-21. Comparison of Stack and Pre-Test Dilution System Blank Results for PM2.5 Semivolatile Organic Species (DRI Sampler, Site Echo).



Notes: (1) Number in parentheses in x-axis labels indicates average stack sample concentration, mg/dscm; (2) ND in x-axis labels indicates substance not detected in blank, detection limit used for ratio.

Figure 2-22. Comparison of Stack and Pre-Test Dilution System Blank Results for Organic PM2.5 Precursors (DRI Sampler, Site Echo).



Notes: (1) Number in parentheses in x-axis labels indicates average stack sample concentration, mg/dscm; (2) ND in x-axis labels indicates substance not detected in blank, detection limit used for ratio.

Figure 2-23. Comparison of Stack and Pre-Test Dilution System Blank Results for Other VOCs (DRI Sampler, Site Echo).

As a rule of thumb, total mass and inorganic stack results that are at least three times the DSB and organic stack results that are at least five to ten times the DSB, and results that are detected in at least three valid test runs, can be considered the most reliable. Stack levels nearer the DSB are not considered robust measurements. PM2.5 mass is two to four times the DSB for most of the runs (Figures 2-19 and 2-20, for the compact and DRI dilution samplers, respectively). Sulfate ion ($SO_4^{=}$) and ammonium ion (NH_4^+) results are generally greater than three times the DSB, whereas most of the other inorganic PM2.5 constituents, EC and OC are not. Semivolatile organic compound (SVOCs) generally (25th to 75th percentile) were detected at levels between one and three times the DSB or MDL, and nearly all (90th percentile) were detected at less than approximately eight times the DSB or MDL (Figure 2-21). Nearly all (90th percentile) of VOCs were detected at less than approximately four times the DSB (Figures 2-22 and 2-23), with only two compounds (2,2-dimethylpentane and 1-pentene) consistently greater than five times the DSB. Thus, quantification of VOCs and SVOCs is highly uncertain at these extremely low concentrations because of significant background levels in the dilution air. DSB results at Site Charlie with the DRI sampler showed generally similar background levels of PM2.5 species and precursors in the dilution air (Figure 2-24). The results indicate the need for further improvements to the dilution air purification system for obtaining reliable measurements at sources with such low concentrations of PM2.5 species and precursors.

SAMPLE COLLECTION AND ANALYSIS ISSUES

Sample collection and analysis methods used in conjunction with the dilution samplers generally followed standard protocols used for ambient air measurements. In general, the methods performed well for the Diesel engine and oil-fired boiler tested in this program, but were challenged by the extremely low concentrations of substances in the exhaust from gas-fired sources.

Elemental and organic carbon

Particulate carbon is a major constituent of ambient PM2.5; therefore, emissions of particulate carbon from mobile and stationary sources are of interest. Early measurements showed that OC comprised the majority of PM2.5 mass emitted from natural gas-fired appliances (Hildemann,

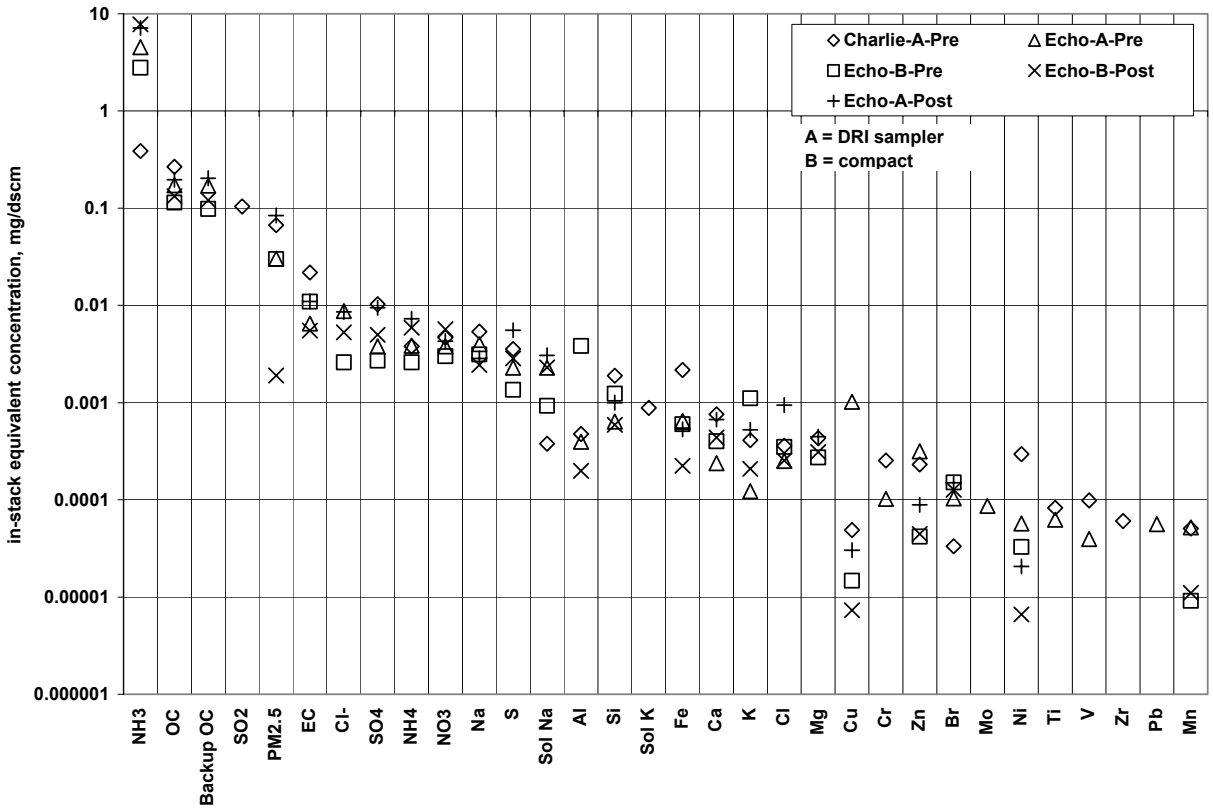


Figure 2-24. Pre-Test and Post-Test Dilution Air Background Concentrations for PM2.5 mass, inorganics, EC and OC (Sites Charlie and Echo).

1991). Subsequent measurements on natural gas and refinery gas-fired industrial stationary sources showed similar composition results (API, 2001a, 2001b, 2001c). OC is the largest component of the PM2.5 mass measured by the dilution sampler for the gas-fired sources tested in this program. However, there are significant questions regarding the reliability of the OC measurements at the extremely low concentrations detected in gas-fired sources. Quartz fiber filters (QFFs) were used to collect PM that was then analyzed for OC and EC by thermal/optical reflectance (TOR) using the IMPROVE protocol. Previous studies have shown that OC measurements on QFFs are susceptible to an artifact: adsorption of VOCs onto the filter media and collected PM, and devolatilization of organic PM, with the adsorptive artifact dominating and causing a positive bias (Mazurek et al., 1993). In this program, a QFF was placed downstream of a Teflon®-membrane filter (TMF) during sample collection and subsequently analyzed for OC and EC to assess the extent of the VOC artifact (Turpin et al., 1994). The OC collected on this filter indicates the potential significance of the VOC artifact relative to the OC

collected on the front-loaded (primary) QFF. This is commonly referred to as "backup OC". In some cases, this approach may overestimate the extent of the VOC artifact because the adsorptive capacity of the filter media itself and the collected particles can affect the amount of VOC adsorbed on the filter (Kirchstetter et al., 2001). Therefore, it is conventional in the open literature not to correct OC measurements for the backup filter/artifact results, but rather to present both sets of results and discuss the potential impact of the VOC artifact on the measured OC results.

To illustrate, Table 2-3 presents data from the backup and primary QFFs for Site Echo, which are typical of the other tests. The corrected OC concentration - i.e., the OC mass measured on the backup QFF subtracted from the OC mass measured on the primary QFF – also is presented to illustrate the potential significance of the VOC artifact. For this test, the backup OC ranges from 59 to 136 percent and averages 99 percent of the primary OC stack results (97 percent of the average stack results). These results are qualitatively similar to the independent results of Hildemann et al. (1991), who determined speciated PM emissions from natural gas-fired home appliances using methods identical to those used in this program. Hildemann found that OC accounted for 84.9 percent of PM mass and that the backup OC accounts for 73 percent of the measured OC emissions, on average. Hildemann's data are incorporated into EPA's SPECIATE database, and are currently the only PM speciation data widely available for gas-combustion. Thus, Hildemann's results provide validation of the OC results measured in this study, and reinforce the need for caution when using the OC results.

Various approaches are under investigation by others to address VOC adsorption artifact. One approach under investigation is to use a denuder to strip VOC from the sample without removing aerosols prior to the filter. However, there is some controversy that this may cause devolatilization OC that is captured on the filter due to equilibrium effects. At this time, no definitive solution has been identified.

Table 2-3. OC and Backup Filter OC Results for Site Echo (mg/dscm).

	Units	Run 1	Run 2	Run 3	Run 4	**Stack Average**	DSB	FB	Trip Blank	Ambient
OC	mg/dscm	2.2E-1	1.6E-1	1.6E-1	2.0E-1	**1.8E-1**	1.7E-1	1.1E-1	9.3E-2	1.1E-2
Backup OC	mg/dscm	1.7E-1	1.5E-1	1.7E-1	1.8E-1	**1.7E-1**	1.7E-1	1.5E-1	1.8E-1	7.0E-3
OC	mg/dscm	1.4E-1	1.0E-1	9.3E-2	5.3E-2	**9.7E-2**	1.1E-1	6.7E-2	--	--
Backup OC	mg/dscm	8.3E-2	8.9E-2	8.7E-2	7.2E-2	**8.3E-2**	9.9E-2	1.2E-1	--	--
OC	mg/dscm	1.4E-1	1.6E-1	1.3E-1	--	**1.4E-1**	2.0E-1	1.1E-1	--	--
Backup OC	mg/dscm	1.3E-1	1.5E-1	1.4E-1	--	**1.4E-1**	2.0E-1	1.5E-1	--	--
OC	mg/dscm	9.2E-2	1.0E-1	1.2E-1	--	**1.0E-1**	1.3E-01	8.3E-2	--	--
Backup OC	mg/dscm	1.2E-1	1.1E-1	1.3E-1	--	**1.2E-1**	1.2E-01	1.5E-1	--	--
Averages:										
OC	mg/dscm	1.5E-1	1.3E-1	1.2E-1	1.3E-1	**1.3E-1**	1.5E-1	9.2E-2	9.3E-2	1.1E-2
Backup OC	mg/dscm	1.2E-1	1.3E-1	1.3E-1	1.3E-1	**1.3E-1**	1.5E-1	1.4E-1	1.8E-1	7.0E-3
OC (corrected for Backup OC)	mg/dscm	2.4E-2	5.2E-3	-8.6E-3	-1.5E-3	**4.2E-3**	5.5E-3	-5.1E-2	-8.3E-2	3.8E-3
Backup OC/OC	%	84	96	107	101	**97**	96	156	189	64

Ultrafine particle characterization

Many epidemiology and toxicology studies are investigating the effect of ultrafine particles (0.1 μm and smaller) on human health, and some believe ultrafine particles may be particularly hazardous. Therefore, there is a need to characterize ultrafine particle emissions (Warren, 2002; HEI, 2002). During the pilot-scale furnace tests (Chang and England, 2004b), an SMPS was used with the dilution sampler to measure ultrafine particle number concentration and size distribution at different points within the dilution sampler for a variety of process and dilution sampler operating conditions. These results were used to develop design and operating specifications for the compact dilution sampler. Similar measurements were made during the Diesel engine test at Site Foxtrot to evaluate the effect of engine configuration and operating conditions on ultrafine particles in the diluted and aged stack gas samples. Exploratory measurements were made in the field during the gas-fired cogeneration plant tests at Site Golf (England et al., 2004) to assess the feasibility of using the instrument at typical stack sampling locations and to obtain preliminary information on ultrafine particle size and number.

In the pilot-scale tests, the SMPS consisted of a differential mobility analyzer (Thermo Scientific Incorporated, TSI, Model 3071) and a condensation nuclei counter (TSI Model 3025). The instrument inlet was connected to the dilution sampler via short length (approximately 4 feet) of Tygon® tubing. In the laboratory setting for the pilot-scale furnace, the SMPS functioned well and results were repeatable for a given test condition. The SMPS was used effectively to evaluate the effects of dilution ratio and residence time on ultrafine particle size for a variety of

exhaust conditions (Chang and England, 2004b). Those studies suggested that ultrafine particles rapidly (between approximately 2 and 10 seconds) equilibrate into larger aerosols with size distributions that are relatively stable after approximately 10 seconds. For residence times of approximately 10 seconds and greater, ultrafine particle size was found to be relatively insensitive to dilution ratio for dilution ratios above approximately 20:1. The effects of other dilution sampling parameters on ultrafine particle size distributions were not investigated directly in this study. It has been extensively reported in the literature on Diesel engine emissions (e.g., Kittelson et al., 2002) that ultrafine particle size distribution can be strongly sensitive to dilution sampling parameters such as dilution ratio, mixing rate, dilution air temperature, relative humidity, sample line length and residence time. An impact of sampling parameters on particle size distribution doesn't necessarily equate to a strong effect on total PM2.5 mass, since most of the mass is represented in the upper end of the size range (0.1 to 2.5 µm) and accumulation of smaller aerosols to larger ones alone has no effect on mass. As discussed earlier, some of the effects reported by Kittelson may be specific to Diesel and reciprocating engines due to the unique history experienced by the combustion gases compared to other types of stationary sources.

Ultrafine particle measurements at Site Foxtrot and in the pilot-scale tests used similar (but not identical) SMPS systems. At Site Foxtrot, replicate measurements were made at 50 and 75 percent engine load in two engine configurations: (a) firing low sulfur Diesel fuel with no post-combustion emission controls (baseline condition); and (b) firing ultra-low sulfur Diesel fuel with a catalytic DPF. Replicate measurements were made in the diluted (approximately 30:1) and aged (approximately 10 seconds) sample for each condition. Under baseline conditions, ultrafine particle number concentration decreased by approximately one third and ultrafine particle size mode decreased slightly from 75-80 nanometers (nm) to 65-70 nm with increasing load. Compared to baseline, ultrafine particle number concentrations with the DPF were much lower, approximately consistent with the high overall reduction in PM2.5 mass (approximately 87 to 89 percent reduction) observed based on filter measurements. In the DPF configuration, ultrafine particle number concentration decreased by approximately one-fourth to more than half and ultrafine particle size mode decreased from approximately 70-75 nm to 55-65 nm with increasing load. It is interesting to note that ultrafine particle number concentrations in the diluted and aged samples were reduced by the DPF, in contrast to some observations for heavy-

duty Diesel engines (Kittelson, 2004). This difference may be a result of the relatively long residence times in the dilution sampler used in these tests.

At Site Golf, a wide range particle sizer (WRPS, MSP Corporation, Model 1000XP, Configuration B) was used. The MSP and the TSI systems employ similar types of components (i.e., differential mobility analyzer (DMA) followed by condensation nuclei counter (CNC)). The WRPS was located on the stack sampling platform with the dilution sampling equipment at approximately 70 feet elevation above grade. The instrument inlet was connected to the dilution sampler via a short length (approximately 4 feet) of Tygon® tubing. The Site Golf test was the first field outing for the brand-new WRPS and the manufacturer's representative assisted with the setup and initial shakedown of the instrument at the site. Valid data were obtained for two of the three test runs. Some operational problems were encountered and solved, but overall the instrument functioned satisfactorily. The results showed peak number concentrations (approximately 1,000 to 40,000 particles per cubic centimeter) occurring in the nucleation mode at approximately 20 nm and peak mass concentrations (approximately 4 micrograms per dry standard cubic meter (μg/dscm)) at approximately 150 nm. The variability of the results was large in the two test runs, with a few individual scans showing significant deviations from the others. The integrated mass concentration equaled approximately one-third of the total PM2.5 mass measured by the integrated filter. Although most of the particles formed during gas combustion are expected to form by nucleation, this indicates that particle growth beyond the ultrafine (0.1 μm and smaller) range may be occurring under these sampling conditions. Note, the results for this site should be considered exploratory; further measurements are needed to corroborate the results.

It should also be noted that the SMPS and WRPS are very expensive research instruments (on the order of $100,000 +/- $30,000) essentially designed for laboratory use. Their ruggedness in repeated field stack sampling use is uncertain, and the costs to maintain proper operation and calibration in this application have not been established. While it was feasible to collect data during the field sampling campaign at Site Golf, the procedures have not been rigorously validated. Further validation of the instrument and sampling procedures is needed. Further development of a ruggedized instrument for stack testing research applications may be needed.

Laser photometer

A laser photometer (TSI DustTrak, Model 8250), also referred to as a nephelometer, was used at Sites Echo and Golf in an attempt to assess PM2.5 concentration trends during the tests. In addition, we wanted to evaluate its use for determining optimum sampling time for minimum integrated filter loadings. At Site Echo, two instruments were used: one connected to the dilution sampler for stack samples and one sampling ambient air near the combustion turbine inlet. The laser photometer inlet was connected to the dilution sampler via a short piece of Tygon® tubing. The stack results from Site Echo did not appear to be valid, since trends appeared to be random and the average PM2.5 response was grossly different from the integrated filter result. No explanation for the Site Echo results was found. At Site Golf, the results were much more promising in that the average PM2.5 response was in fair agreement with the integrated filter result, and trends seemed more reasonable. Further evaluation of the instrument is needed for qualitative and quantitative applications.

DILUTION METHOD

The test procedures outlined previously are being developed as an ASTM standard. The standard is intended for characterization of total PM2.5 mass. The standard is intended to be performance based, since equipment development is still in the early stages and no commercial systems are currently available. In addition to these performance criteria (e.g., residence time, materials of construction, etc.), the standard will seek to identify dilution conditions (e.g., dilution ratio, residence time, temperatures, etc.) needed to obtain repeatable results and goals for precision and accuracy. Dilution ratio and residence time requirements are based on the pilot-scale furnace tests discussed previously. Other considerations are discussed below. Because data for oil-fired sources is limited to four test runs at a single site, the discussion is focused on gas-fired sources.

Effect of Dilution Conditions: Relative Humidity

Studies to characterize effects of dilution conditions on Diesel particulate measurements suggest that relative humidity can affect ultrafine particle size distribution (e.g., Samaras, 2002). Although it is clear that humidity can strongly influence ultrafine particle size distribution

because it can enhance agglomeration and condensational growth in an environment of changing temperatures and concentrations, its effect on total PM2.5 mass may be less significant in this test program. Based on prior studies of inorganic salt particle deliquescence and recrystallization, the impact of raising the relative humidity is expected to have no impact on salt particle size up to approximately 70 percent relatively humidity (Figure 2-25). The effect for sulfuric acid (H_2SO_4) aerosol, which is hygroscopic, also is expected to be relatively small up to approximately 80 percent relative humidity. Both of these effects should have minimal impact on sample mass when samples are conditioned at low relative humidity prior to weighing since any gained moisture due to deliquescence or hygroscopicity should be released. Controlled tests to evaluate the effects of relative humidity were not performed in this program. However, no apparent correlation was observed between PM2.5 mass and the relative humidity of either the diluted sample (Figure 2-26) or the dilution air (Figure 2-27) among the various gas-fired unit tests. This seems reasonable if one assumes that the hygroscopicity of the particles from gas combustion is low and that any excess free moisture is eliminated during sample analysis (filters were equilibrated for at least 24 hours at 20 ºC and 30±5 percent relative humidity prior to weighing). Therefore, relative humidity of the diluted sample and the dilution air does not appear to be of first-order importance for gas-fired sources within the range of conditions in this program. As other sources of variation become better understood, relative humidity could become more important and, if so, should be systematically evaluated under controlled conditions in future tests.

Effect of Dilution Conditions: Temperature

Recent studies of Diesel engine exhaust suggest that dilution air temperature and sample filter temperature can affect fine particle mass and size measurements (e.g., Kittelson, 2002; Samaras, 2002). Controlled tests to evaluate these effects for the types of sources tested in this program were not performed. Examining the results from all the gas-fired sites tested in this program suggests there may be a very weak relationship between PM2.5 concentration and temperature of the dilution air (Figures 2-28). While Kittelson's results showed a decrease in particulate concentration with increasing dilution air temperature, Figure 2-28 suggests a possible increase in particulate concentration with increasing dilution air temperature. This effect should be evaluated in controlled tests since temperature was not the only variable among the tests. There

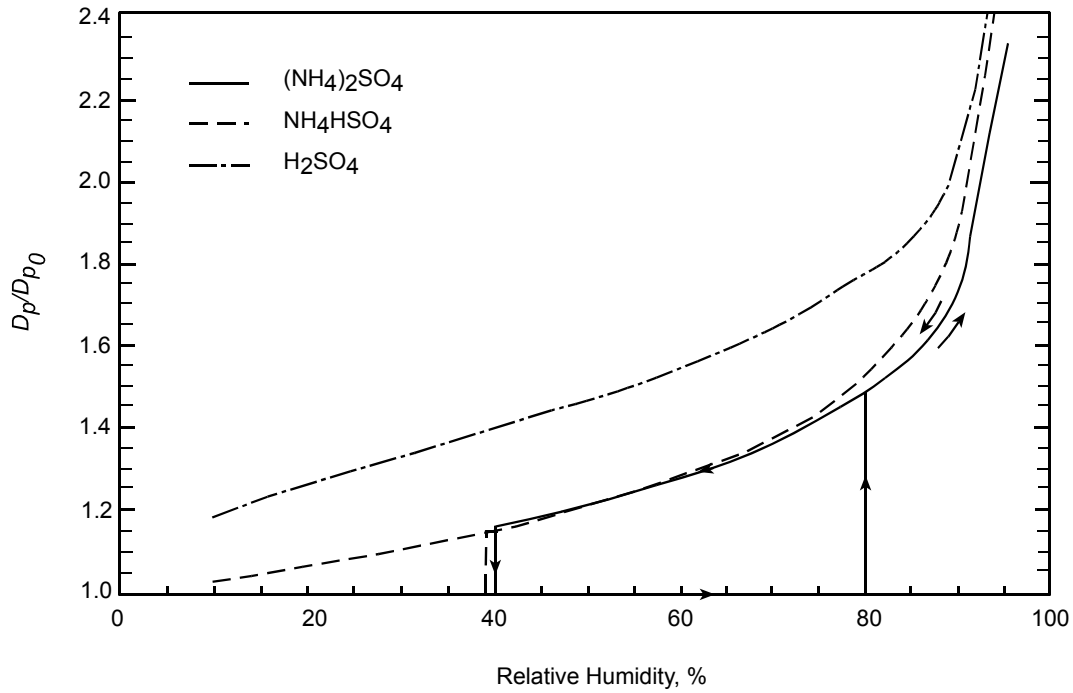


Figure 2-25. Effect of Relative Humidity on Particle Diameter (Seinfeld and Pandis, 1998).

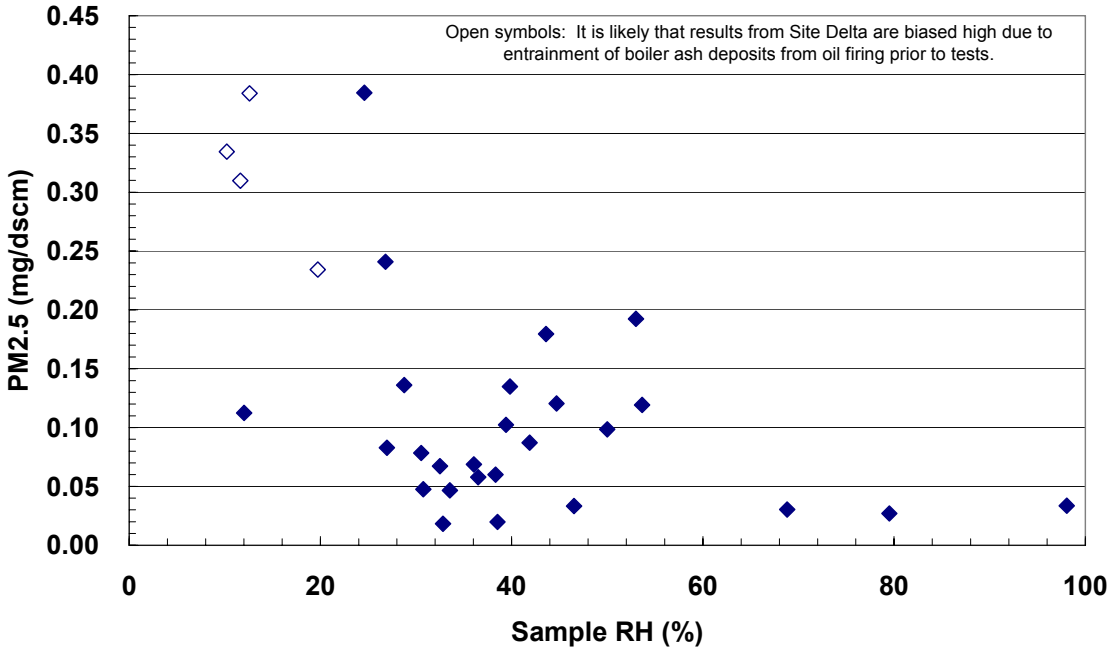


Figure 2-26. Measured PM2.5 concentration versus Relative Humidity of Diluted Sample (All Gas Fired Sites).

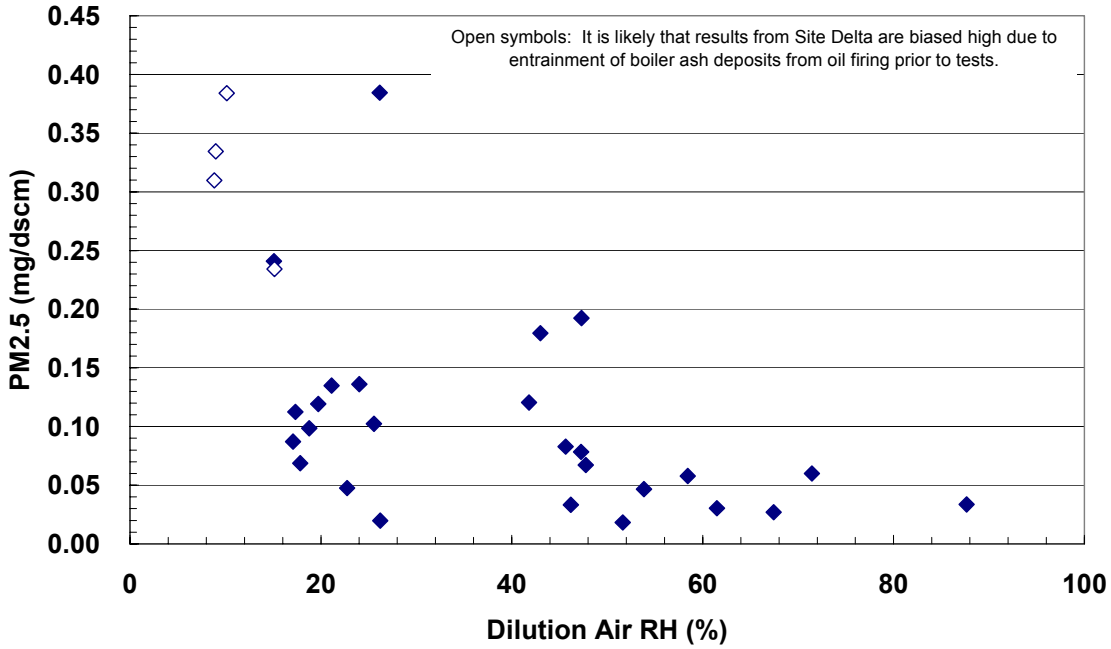


Figure 2-27. PM2.5 versus Dilution Air Relative Humidity (All Gas-Fired Sites). Temperature

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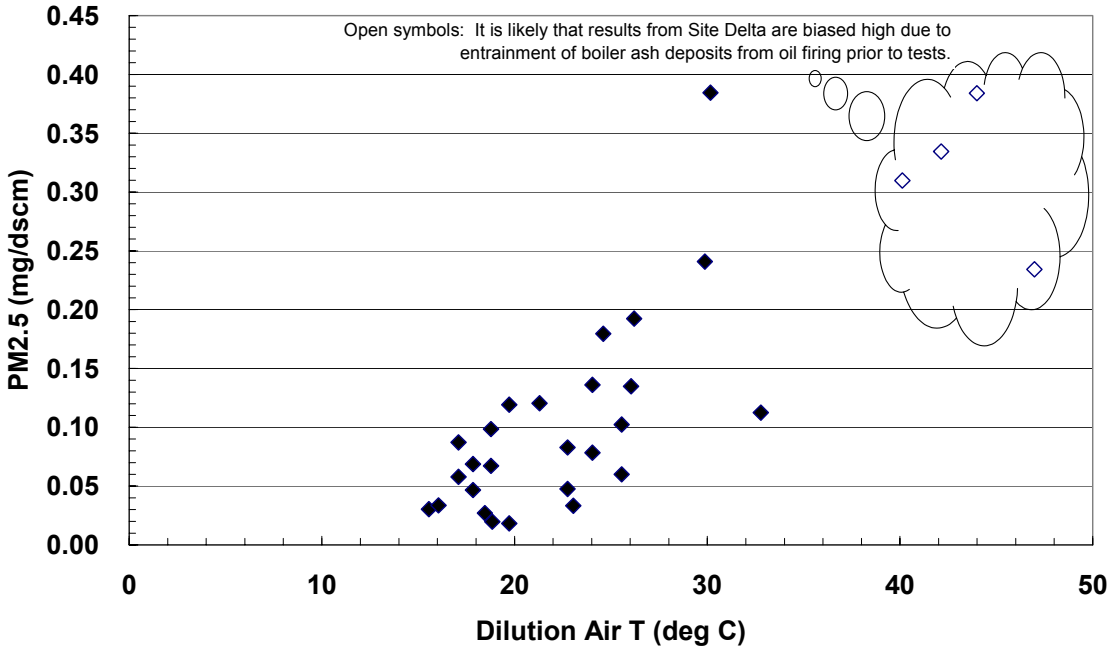


Figure 2-28. PM2.5 versus Dilution Air Temperature (All Gas-Fired Sites).

is no apparent relationship between PM2.5 and sample temperature (Figure 2-29). It is likely that these differences in behavior are due to much lower concentrations of condensable vapors and carbonaceous nucleation sites for these sources compared to Diesel engines. This suggests particle volatility over the range experienced in these tests is not a key factor for measurements on gas-fired sources. Based on these results, it does not appear necessary at this time to specify tight limits on either dilution air temperature or sample filter temperature for measurements on gas-fired sources

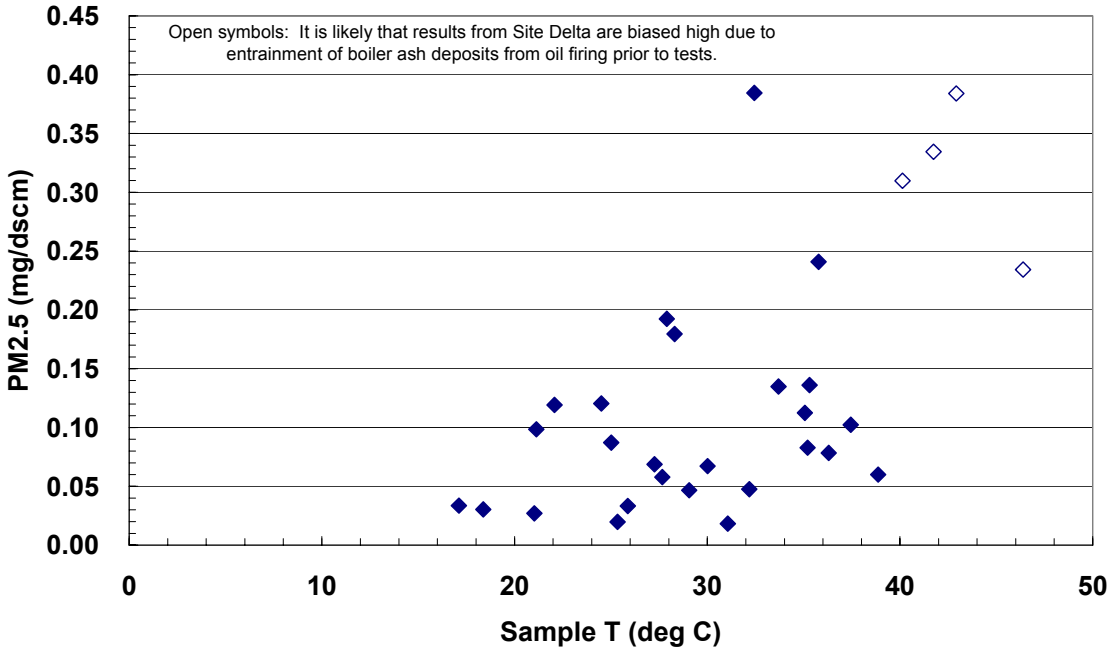


Figure 2-29. PM2.5 versus Sample Temperature (All Gas-Fired Sites).

Effect of Dilution Conditions: Dilution Ratio

The pilot-scale furnace tests (Chang and England, 2004b) suggested that PM2.5 concentration should be relatively independent of dilution ratio for residence times of at least ten seconds and dilution ratio of 20 and higher. Dilution ratio was not varied for controlled conditions during the field tests, but dilution ratio did vary from site to site and in some cases run to run. There is no apparent correlation between PM2.5 concentration and dilution ratio among results for the gas-fired sites (Figure 2-30). Thus, it does not appear necessary to specify an upper limit to dilution ratio for measurements on gas-fired sources at this time.

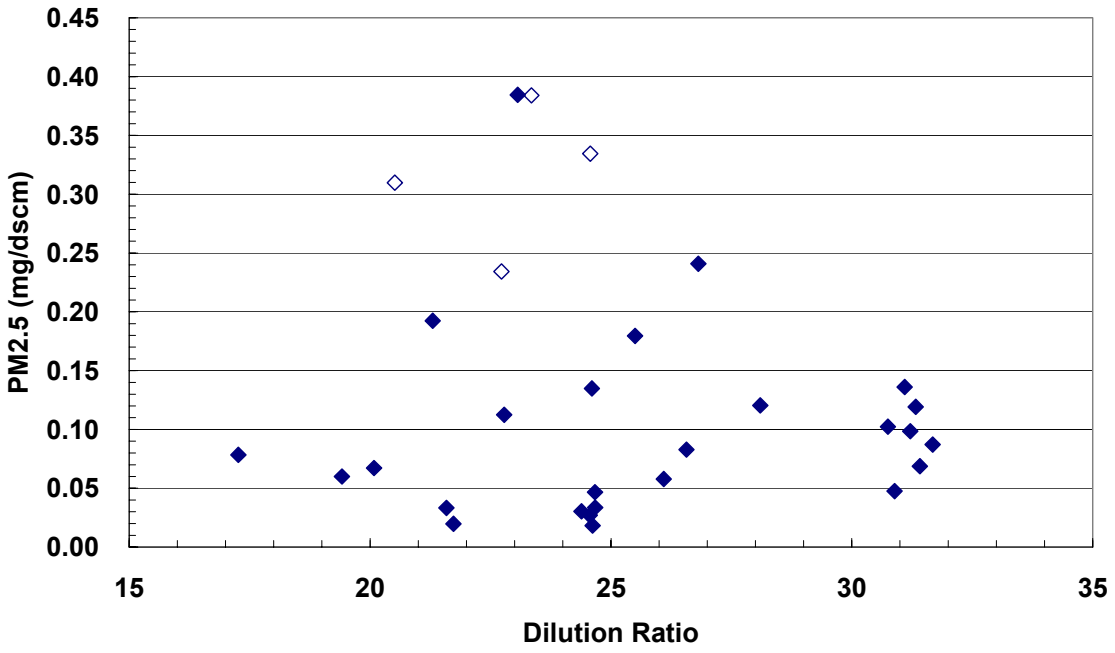


Figure 2-30. PM2.5 versus Dilution Ratio (All Gas-Fired Sites, DRI and Compact Samplers).

Accuracy and Precision of PM2.5 Measurements

The results of the program enable a limited assessment of accuracy (systematic variation) and precision (random variation) of the dilution sampling method with the equipment used in this program.

Accuracy or systematic variation is characterized by the difference between a result and the true value. Accuracy of a stack test method can be defined by two different approaches: comparison to an existing reference method or analyte spiking (U.S. EPA, 1992). Analyte spiking at levels typical of the gas-fired units tested in this program was considered beyond the scope of the present program due to the equipment required to generate suitable aerosol concentrations. Dynamic analyte spiking tests were performed during the pilot-scale furnace tests with H_2SO_4 and zinc oxide particle injection into the furnace to generate elevated concentrations of condensable and solid aerosols comparable to oil- and coal-fired boilers. However, quantitative assessment of the spike recovery in the sampler was not possible due to particle deposition and reactions in the furnace prior to the sampling location. Hildemann et al. (1989) spiked the dilution sampler with monodisperse ammonium fluoroscein particles and determined the

recovery efficiency (fractional particle losses) through the different sections of the sampler as a function of particle size (see earlier Figure 2-4). These results showed that accuracy of the Hildemann dilution sampler for PM2.5 is probably better than ±3 percent provided deposits in the sample probe and venturi are recovered. Since the Hildemann dilution sampler (and its DRI derivative) is well characterized, it was considered suitable as a reference for assessing the accuracy of the compact sampler.

Comparison tests were conducted with the DRI and compact dilution samplers at Site Foxtrot (backup generator Diesel engine). For PM2.5 concentrations of approximately 3.2 mg/dscm (Diesel engine with DPF), the Site Foxtrot results indicated a negligible average PM2.5 mass bias of -2 percent (0.07 mg/dscm) in the compact sampler relative to the DRI dilution sampler, and that this bias is not significant at the 95 percent confidence level given the uncertainty of the results (Figure 2-31). This includes deposits on the sample filter plus deposits recovered from the sample probe, sample transfer line and venturi. Tests were also conducted at a PM2.5 concentration of approximately 22 mg/dscm (Diesel engine without DPF), but the compact sampler results are not valid due to a measurement error.

Total PM measurements also were made at site Foxtrot using a dilution system according to ISO 8178 (1996a, 1996b) requirements, albeit on different days at identical engine operating conditions. The DRI dilution sampler showed a bias ranging from –11 to +9 percent (Table 2-4) at the high PM2.5 concentration relative to the ISO method results, but the differences are within the 95 percent confidence intervals (approximately two standard deviations) of the mean results so the bias is not significant at this confidence level. At the lower PM2.5 concentration, the DRI and compact dilution samplers showed a bias ranging from -24 to –27 percent compared to the ISO method results and the differences are larger than the 95 percent confidence intervals. The ISO method measured total PM, whereas the DRI and compact dilution samplers measured only the PM2.5 fraction of total PM, so it is likely this explains at least part of the difference between the measurements. Further tests are needed to confirm these results and determine if the differences are repeatable.

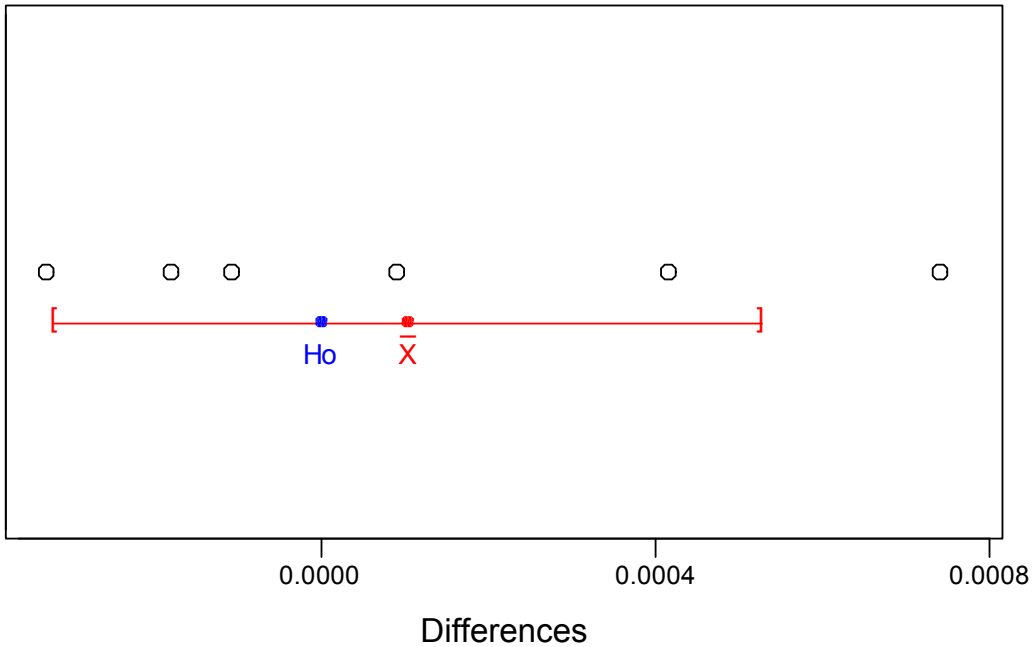


Figure 2-31. Paired Sample t-Test results for DRI and Compact Sampler PM2.5 Mass Results at Site Foxtrot (With Null Hypothesis, H_0, and 95% t-Confidence Interval for the Mean).

Table 2-4. Comparison of ISO 8178, DRI and Compact Dilution Sampler PM Results for a Diesel Engine (Site Foxtrot).

	Total PM, mg/dscm		PM2.5, mg/dscm			
	ISO mean	ISO stdev	DRI mean	DRI stdev	Compact mean	Compact stdev
Base, 50% load	30.2	1.52	26.9	1.92	nv	nv
Base, 75% load	30.6	1.48	33.5	9.71	nv	nv
DPF, 50% load	5.30	0.20	4.01	0.06	3.85	0.45
DPF, 75% load	4.33	0.25	3.26	0.08	3.28	0.22

Base = baseline (no emission controls) and California Diesel fuel.
DPF = Diesel particulate filter and ultra-low sulfur Diesel fuel.
nv = not valid

Comparison tests also were performed at Site Echo (natural gas-fired power plant) using the DRI and compact dilution samplers at a measured (uncorrected) stack PM2.5 concentration on the order of approximately 0.1 mg/dscm (see earlier Figure 2-16). It should be noted that analysis of the results suggests the MDL for the dilution method as applied to gas-fired sources in this test program is probably on the order of 0.05 mg/dscm. Based on the PM2.5 results presented earlier in Figure 2-13, the compact sampler PM2.5 results have an average bias of approximately –6 percent compared to the DRI dilution sampler. This difference is not significant at the 95

percent confidence level. Note, these results exclude the acetone rinses of the probe and sample venturi because those results are completely masked by background levels at the low stack PM2.5 concentrations at this Site. Based on Hildemann's (1989) results, this should have small impact on the results assuming most of the mass is represented in particles smaller than 2 μm.

Measurement precision or random variation is characterized by the standard deviation for a population of results. Over the course of this program, precision improved as the test team gained experience with the equipment and as insights and problems led to improved procedures. For example, Figure 2-32 shows stack PM2.5 results for gas-fired sources chronologically for the present program and its predecessor. The error bars represent the 95 percent confidence interval, incorporating variability due to measurement, process and other sources of imprecision. Except for Sites Charlie and Bravo, where a procedural error (overtightening of filter cassettes) led to unusually poor precision, precision improved with time. The average 95 percent confidence interval (2 standard deviations) for a three to four run test improved from approximately ±0.14 mg/dscm (or ±85 percent of 0.16 mg/dscm) in 1998-1999 to approximately ±0.05 mg/dscm (or ±52 percent of 0.1 mg/dscm) in 2003. It should be noted that these values represent conservative estimates of measurement precision since they include the combined variability in the measurements, the process, and external factors. Measurement variability is believed to dominate precision in most cases.

Precision for oil combustion is based on a smaller data set obtained from Sites Delta and Foxtrot (Figure 2-33). For tests of the oil-fired boiler at Site Delta, the 95 percent confidence interval of the measurements was ±6.5 mg/dscm (or ±45 percent) at a mean stack PM2.5 of approximately 14 mg/dscm. Subsequent tests on a Diesel engine at Site Foxtrot without emission controls showed a 95 percent confidence interval of ±4 and ±19 mg/dscm (±14 and ±58 percent) for two different test sets at a mean stack PM2.5 concentration of approximately 30 mg/dscm. The higher value seems atypical compared to the other five test sets at this site, and suggests that some portion of the measurement process remains uncontrolled, however no explanation for the difference was identified. The final series of tests at Site Foxtrot showed an average 95 percent confidence interval of approximately 0.4 mg/dscm (±11 percent) for four different test sets at a mean PM2.5 concentration of approximately 4 mg/dscm. The average relative precision for five of the six test sets at Site Foxtrot is ±12 percent. Again, these values represent conservative

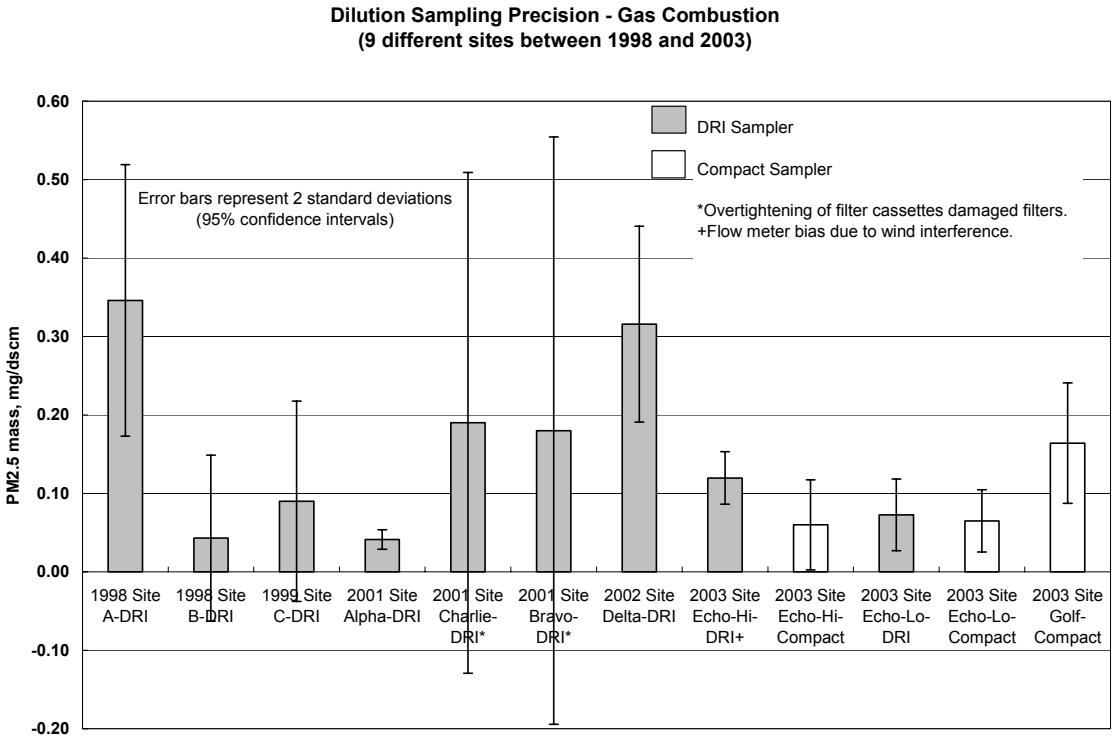


Figure 2-32. Dilution Sampling PM2.5 Precision for Gas-Fired Sources.

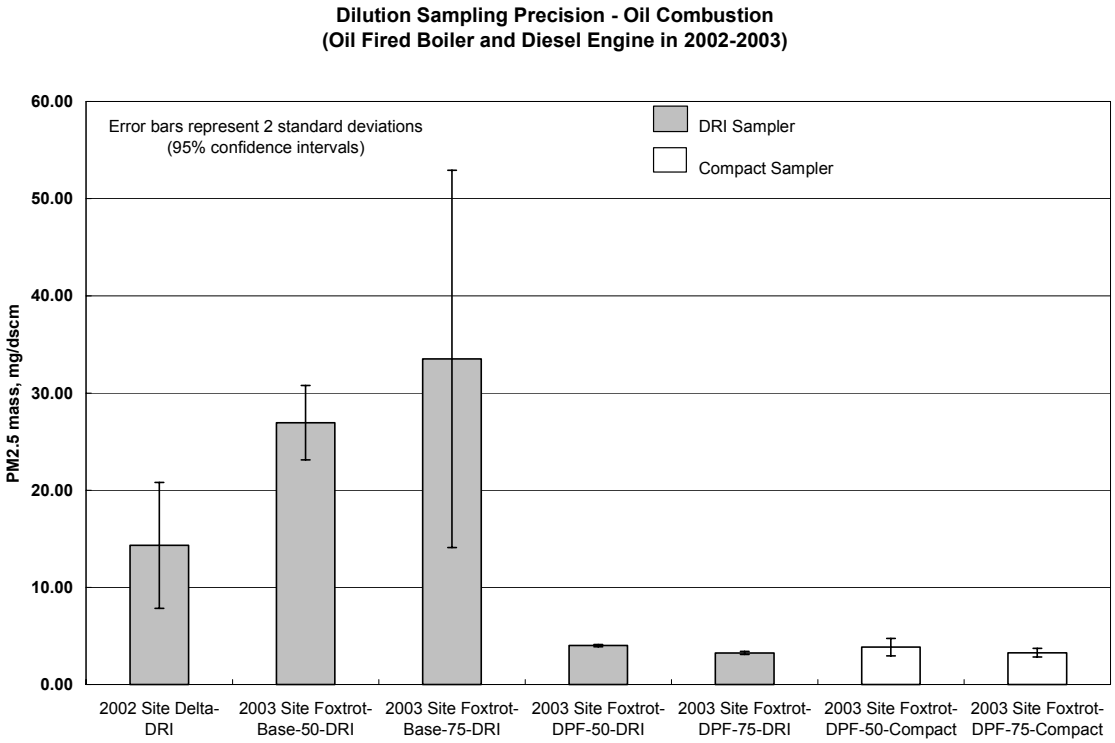


Figure 2-33. Dilution Sampling Precision for Oil-Fired Sources.

estimates of measurement precision since they include the combined variability in the measurements, the process, and external factors.

From these results, it is clear that more tests are needed before robust values can be assigned to dilution method accuracy and precision. The limited results in this program suggest that accuracy relative to the DRI benchmark of two to six percent is achievable for PM2.5 concentrations ranging from approximately 0.1 to 3 mg/dscm. Comparison of the DRI and compact sampler results to ISO 8178 results indicate a potential bias of –9 to –27 percent at PM2.5 concentrations from approximately 3 to 30 mg/dscm on a Diesel engine. Further tests are needed to confirm these results. The range of precisions in several of the tests indicates there may be some parts of the measurement process that are not under control. Some of the test results suggest that 95 percent confidence intervals as low as approximately 12 percent may be achievable for PM2.5 concentrations of approximately 3 mg/dscm and greater. In tests on the Diesel engine at Site Foxtrot, the precisions of the DRI and compact dilution samplers and the ISO Method 8178 dilution sampling system were the same (based on statistical F-test at 95 percent confidence level). For low PM2.5 concentrations characteristic of gas combustion (approximately 0.05 to 0.3 mg/dscm), 95 percent confidence intervals from ±28 to more than ±200 percent were observed, with most of the results for each test set between ±41 and ±87 percent (25th to 75th percentile).

TESTING COST

The cost of testing for PM2.5 mass was estimated for comparison to typical current particulate testing costs. It is assumed that test procedures are established, test crews are trained and experienced with the method, and commercially manufactured equipment would have simplified operating procedures (e.g., more sophisticated software and controls reducing the number of manual calculations and adjustments needed during the test, such that the system can reasonably be operated by a qualified source test individual). Interviews with the test team in this program were conducted to assess the complexity of tests using the compact sampler relative to EPA Method 5 and 202 (U.S. EPA, 1996a, 1996b). The final test of the program (Site Golf), where only the compact sampler was used with a minimal scope of PM2.5 speciation, represents the closest to a routine application of the method with the exception of long (six-hour) test runs.

Based on an activity log of those tests, it was estimated that three 2-hour test runs could be completed in a single 12- to 13-hour test day. This served as the basis for the estimated testing costs.

Equipment Costs

The cost for a dilution sampler was estimated based on the current compact sampler design (Table 2-5). The "first unit" cost, including initial design drawings and software configuration and assuming highly skilled labor resources, is used as a very conservative estimate of near-term costs. The cost of the 100th manufactured unit produced by a typical stack test equipment supplier could reasonably be expected to be much less, typically one half to one third of the first unit cost, due to typical economies of scale. The equipment cost per day of testing is calculated assuming straight-line depreciation of capital expense over 5 years. Annual capital depreciation is assumed amortized through equipment rental fees applied over 2 months (assuming weekdays only, a total of 43 days), or 17 percent equipment utilization over the course of a year. Annual maintenance and calibration costs are assumed at 20 percent of the parts, equipment, instrumentation and control equipment costs.

Overall Test Costs

Overall testing costs for 2-hour test runs were estimated for a 2-day test schedule, with off-site preparation on the first day and setup and testing at the field site on the second day (Table 2-6). The following assumptions are made:

- The site is within 1-hour driving distance of the tester's base;
- Sample collection and analysis for PM2.5 mass only;
- The target in-stack LQL for PM2.5 mass is approximately 0.6 mg/dscm (based on dilution air background), or, if dilution air background can be eliminated, as low as 0.06 mg/dscm (based on analytical uncertainty). Refer to Figure 2-18;
- Analytical costs assume that only the PM2.5 fraction is analyzed (in-stack cyclone catch discarded or archived);

Table 2-5. Estimated Dilution Sampler First-Unit Equipment Cost.

Cost Element	Labor*	Non-Labor	Total
First unit costs			
Design/drawings	$ 6,000		$ 6,000
Sourcing	$ 2,600		$ 2,600
Software	$ 8,000		$ 8,000
Production Costs			
Procurement	$ 1,000		$ 1,000
Raw materials		$ 514	$ 514
Parts & equipment		$ 9,449	$ 9,449
Instrumentation & controls		$ 7,948	$ 7,948
Fabrication	$ 7,700		$ 7,700
Assembly	$ 6,600		$ 6,600
Quality control	$ 4,400		$ 4,400
Shipping/Handling (FOB)		$ 300	$ 300
Subtotal	$ 36,300	$ 18,210	$ 54,510
Indirect Costs - Non-Labor (15%)		$ 2,732	$ 2,732
Total	$ 36,300	$ 20,942	$ 57,242
Annual Maintenance and Calibration**			$ 3,479
Annual Depreciation (5 years)			$ 11,448
Total Annual Cost			$ 14,928
Testing days per year			43
Cost per test day			**$ 347**

*assumes fully burdened rate of $100 per labor hour.
**Assumes 20 percent of parts & equipment, Instrumentation and Controls cost.

- The sampler is modified to generate DSBs concurrently with all three test runs;
- One filter blank and one acetone recovery blank are analyzed for quality assurance/quality control (QA/QC); and
- Filter gravimetric analysis is conducted by an EPA research laboratory contractor using standard operating procedures consistent with those being used for PM2.5 ambient monitoring stations.

Table 2-6. Estimated Dilution Sampling Test Program Cost (2-Hour Test Runs).

	Day	Clock Time Start	Labor Hours	Labor Rate*	Labor Cost, $	Non-Labor Unit Cost	No. of Units	Non-Labor Cost, $	Non-Labor Burden (15%)	Total, $
Test Plan			2	$ 75.00	$ 150.00				$ -	$ 150.00
Mobilization	1									
Supplies-Filters	1				$ -	$ 18.86	7	$ 132.00	$ 19.80	$ 151.80
Supplies-Other	1				$ -	$ 25.00	11	$ 275.00	$ 41.25	$ 316.25
Cleaning	1		4	$ 50.00	$ 200.00	$ 50.00	1	$ 50.00	$ 7.50	$ 257.50
Packing/Shipping	1		2	$ 50.00	$ 100.00			$ -	$ -	$ 100.00
Travel	2	7:00	2	$ 50.00	$ 100.00	$ 0.35		$ -	$ -	$ 100.00
Setup	2	8:00	4	$ 50.00	$ 200.00			$ -	$ -	$ 200.00
Sample Collection	2									
Supplies	2					$ 100.00	1	$ 100.00	$ 15.00	$ 115.00
QA Checks	2	10:00	1	$ 50.00	$ 50.00			$ -	$ -	$ 50.00
Sample Collection-Run 1	2	10:30	4	$ 62.50	$ 250.00			$ -	$ -	$ 250.00
Turnaround	2	12:30	1	$ 75.00	$ 75.00			$ -	$ -	$ 75.00
Sample Collection-Run 2	2	13:00	4	$ 75.00	$ 300.00			$ -	$ -	$ 300.00
Turnaround	2	15:00	1	$ 75.00	$ 75.00			$ -	$ -	$ 75.00
Sample Collection-Run 3	2	15:30	4	$ 75.00	$ 300.00			$ -	$ -	$ 300.00
Sample Recovery/Blanks	2	17:30	1	$ 75.00	$ 75.00			$ -	$ -	$ 75.00
Travel	2							$ -	$ -	$ -
Demobilization	2									
Packing/Shipping	2	18:45	4	$ 75.00	$ 300.00			$ -	$ -	$ 300.00
Travel	2	19:50	2	$ 75.00	$ 150.00			$ -	$ -	$ 150.00
Sample Analysis										
Filters - Gravimetric**						$ 234.86	7	$ 1,644.00	$ 246.60	$ 1,890.60
Acetone - Gravimetric						$ 50.00	4	$ 200.00	$ 30.00	$ 230.00
Report										
Data reduction			8	$ 75.00	$ 600.00			$ -	$ -	$ 600.00
Report Preparation			8	$ 75.00	$ 600.00			$ -	$ -	$ 600.00
Equipment						$ 362.28	1	$ 362.28		$ 362.28
Total			**52**		**$ 3,525.00**			**$ 2,763.28**	**$ 360.15**	**$ 6,648.43**

*Fully burdened, straight time.
**Assumes 1 sample plus 1 DSB per test run, plus 1 filter trip blank.

3. PM2.5 EMISSION FACTORS AND SPECIATION PROFILES

The purpose of this section of the report is to develop composite PM2.5 emission factors derived from results of dilution sampling tests in this program and the prior API program for gas- and oil-fired sources. Emission factors are a cost-effective means of developing area-wide emission inventories, which are one of the fundamental tools for air quality management. They also are useful for estimating emissions impacts of new facilities. In response to requests from the U.S. Congress and the U.S. EPA, the National Research Council established the Committee on Research Priorities for Airborne Particulate Matter. The blue-ribbon panel of experts from industry, academia and the regulatory community identified that characterization of source emissions—especially the size distribution, chemical composition, and mass emission rates of PM, and the emissions of reactive gases that lead to secondary particle formation through atmospheric chemical reactions—is one of the ten key national research priorities (NRC, 1999). Emission factors were derived from the results of this test program to facilitate data analysis and application.

It should be noted that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source PM10 emission standards or permit limits. Widely accepted, standardized procedures for stationary source dilution sampling do not currently exist. Dilution sampling has not been fully validated for use on all stationary sources. Therefore, data users should apply appropriate caution when using these results. Recently, EPA published a conditional test method (CTM-039) for stationary source dilution sampling and conducted limited tests on coal- and oil-fired boilers (U.S. EPA, 2003a). EPA proposed the method as an alternative for testing needed to develop PM2.5 emission inventories (U.S. EPA, 2003b). While the equipment and procedures specified in the method differ from those used in this program, it indicates such methods may become more generally accepted in the future.

PM2.5 EMISSION FACTOR DEVELOPMENT

PM2.5 emission factors were determined by dividing the emission rate, in pounds per hour (lb/hr), by the measured heat input, in million British thermal units per hour (MMBtu/hr), to give pounds per million British thermal units (lb/MMBtu) for each test run within a source category. Heat input is the product of the measured fuel flow rate and the average fuel heating value, obtained from the plant process data. Average emission factors for each source category were then determined in three steps:

- First, the data set was tested for normality using the Anderson-Darling test. Environmental data sets are often lognormal (U.S. EPA, 2000). If the data set was not normally distributed at the 95 percent confidence level, it was assumed to be lognormal, transformed (by taking the log of the value), and tested again. If the test showed the distribution to be lognormal, the transformed data set was used in the next steps. All data sets for each source category tested either normal or lognormal, so other probability distributions were not tested.

- The lowest and highest points in a data set (raw or transformed) were tested for outliers using the extreme value (Dixon's) test, which is appropriate for data sets with 25 or fewer data points. If the lowest or highest point was determined to be an outlier, the next lowest or highest values were also tested, and so forth, to determine all outliers in the set. Each outlier was investigated to determine if there was a valid reason to exclude it; if so, the outlier was deleted before performing the next steps. Otherwise, the data were retained in the data set.

- The average emission factor was determined by taking the arithmetic mean of the raw (untransformed) data set for all valid test runs. Since the arithmetic mean is sensitive to data extremes, it provides a conservative estimate of emissions. The variability of the mean is described by the uncertainty at the 95 percent confidence level, as described below.

Treatment of Results Below Detection Limits

Undetected data for PM2.5 mass and species are excluded from calculations. This treatment of undetected data differs from the procedure used by EPA for development of emission factor documents (U.S. EPA, 1997b), in which one-half of the MDL is substituted for undetected data and used in sums and averaged data. The MDL is a measure of measurement noise. The approach used in this report was chosen to avoid ambiguity when applying the results for source apportionment analysis.

Because one-half the detection limit is not included in the average results and uncertainty cannot be determined based on a single datum, species mass fractions and PM2.5 gaseous precursors are reported for only those substances detected in at least two test runs at each individual source. Species mass fractions based on data detected in at least three test runs are considered the most reliable.

Uncertainty and Representativeness

As a measure of emission factor reliability, the bias (accuracy or systematic uncertainty) and precision (variability or random uncertainty) of the results, the total relative uncertainty (at the 95 percent confidence level) and 95 percent confidence upper bound were calculated for each emission factor and mass fraction using standard error analysis procedures (American Society of Mechanical Engineers (ASME), 1990). The total emission factor uncertainty includes uncertainty in the sample volumes, dilution ratios, fuel flow rate, fuel heating value and run-to-run variability in addition to the analytical uncertainty. The total relative uncertainty represents the 95 percent confidence interval based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level. Uncertainties for each individual source were combined for a source category average by addition in quadrature.

The uncertainty for the full data set in each source category was recalculated using the results for each individual test run. The relative bias and precision of sample analysis, flue gas flow rate measurements, heat input and sum of species for each site were combined for the recalculated uncertainty by addition in quadrature.

Many of the reported emission factors derived from these results have high uncertainty. Run-to-run variability dominates random uncertainty, which in turn dominates total uncertainty in most cases. The high uncertainty in these tests is attributed to the very low pollutant concentrations present in the samples—at or near the ability of the methods to detect them—and to slightly different operating conditions for each test run. Emission factors for substances detected in at least three valid test runs are considered to be the most reliable; those detected in fewer than three test runs at an individual source are considered less reliable (not suitable for quantitative analysis) and are grouped separately in the tables. Relative uncertainty greater than 100 percent

indicates it is likely that actual emissions are different from the reported value, and they cannot be distinguished from zero or MDL with high confidence. Emission factors with an uncertainty greater than 100 percent should be considered potentially unrepresentative and data users should apply appropriate caution when using them. A large relative uncertainty does not necessarily imply the results are of no value. Although the absolute value of the emission factor is therefore uncertain, the 95 percent confidence upper bound represents a plausible upper bound for emissions (i.e., it is likely that the actual emissions are below the upper bound). Because of the small number of individual source tests, the reported uncertainty and average results do not include the potential uncertainty associated with all plant configurations, operating conditions, geographical locations, fuel variations, etc.

Emission Factor Quality

These tests represent one of the first applications of dilution sampling to these types of sources and fuels, and, in many cases, the extremely low concentrations of PM and other pollutants challenged the limits of the state-of-the-art methods employed.

In some cases, all of the emission measurements made at the stack were downstream of supplementary burners and/or post-combustion air pollution controls. Therefore, results from these sources do not represent emissions from the primary equipment (e.g., gas turbine) alone. In some cases, the operating conditions for each individual test varied with normal plant operation near full load (see individual source test reports for further details). Therefore, the resulting emission factors are not considered representative of any particular operating condition but rather are the average of the operating conditions during these tests. Consequently, data users should apply considerable caution when using these results.

Emission factors derived from a test of a single unit should be used with considerable caution. Such results do not necessarily represent results from a random sample of an entire source category population due to differences in design, configuration, emission controls, maintenance condition, operating conditions, geographic location, fuel compositions, ambient/weather conditions and other factors. The emission factors derived from this test should not be considered representative of all units within the same source category, and may best be used in

conjunction with test results from other units within the same source category population to develop more robust, reliable emission factors.

The dilution sampling and sample collection/analysis methods used in this program are well documented in the peer-reviewed scientific literature and/or in published EPA test methods and protocols. Moreover, the test methods and data quality are extensively documented in each individual test report, in sufficient detail for others to reproduce the tests. However, it is emphasized that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source PM10 emission standards or permit limits. Widely recognized standard methods for stationary source dilution sampling do not presently exist.

The quality of the emission factors derived from this test should not be considered high because the emission factors are based on a single test or a single unit that may not be representative of the entire source category population. This does not mean that these test results are not of value or high quality, but rather indicates that more tests are needed to corroborate the results before they are widely applied. As noted above, the emission factors derived from these test results may best be used in conjunction with test results from other units within the source category population to develop more robust, reliable emission factors.

DATA SOURCES AND CATEGORIES

Data used for development of PM2.5 emission factors and speciation profiles based on dilution sampling were drawn from the data sources listed below. Standard U.S. EPA Source Classification Codes—SCC—are provided for each source. In some cases a source falls into more than one SCC. In these cases, the most specific SCC is listed in bold type.

- External combustion – gas fuel
    - API-DOE PM2.5 Program, Site A (Boiler, refinery fuel gas, SCC 10200701)
    - API-DOE PM2.5 Program, Site B (Process Heater, refinery fuel gas; SCC 30600102, 30600104, **30600106**)

- API-DOE PM2.5 Program, Site C (Steam Generator, Natural Gas; SCC 31000414)
- GRI-DOE-API Program, Site Alpha (Refinery Process Heater, Refinery Fuel Gas; SCC 30600102, 30600104, 30600106)
- GRI-DOE-API Program, Site Charlie (Refinery Process Heater, Natural Gas; SCC 30600102, 30600104, **30600105**)
- GRI-DOE-API Program, Site Delta (Institutional Boiler, Natural Gas, SCC 10300601)

- External Combustion – No. 6 Fuel Oil
  - GRI-DOE-API Program, Site Delta (Institutional Boiler, SCC 10300401)
- Internal Combustion – Reciprocating Engines
  - GRI-DOE-API Program, Site Foxtrot (Backup Diesel Generator; SCC 20100102, 20100107)
- Internal Combustion –Combined Cycle/Cogeneration
  - GRI-DOE-API Program, Site Bravo (Combined Cycle/Cogeneration Plant, Natural Gas; SCC 20100201, 20100209, **20200203**)
  - GRI-DOE-API Program, Site Echo (Combined Cycle/Cogeneration Plant, Natural Gas; SCC 20100201, 20100209, **20200203**)
  - GRI-DOE-API Program, Site Golf (Cogeneration Plant, Refinery Fuel Gas; SCC **20200203**)

The scope of data sources was limited to the six gas-fired sources tested in the current project plus three gas-fired sources tested in a predecessor project using the same or similar dilution sampling equipment and procedures because the procedures and quality assurance results are well documented.

PM2.5 EMISSION FACTORS

PM2.5 mass emission factors are presented below for each of five source categories:

- Gas-Fired Boilers
- Gas-Fired Process Heaters
- Gas-Fired Combined Cycle and Cogeneration Plants
- Oil-Fired Boilers
- Diesel Engines

It should be noted that all of the data sets have statistically small populations (less than 30 data points). For the reasons noted earlier, these factors may not be representative of either the sources tested or the entire population of a source category or any particular operating conditions.

Gas-Fired Boilers

Data from the two gas-fired boilers and one natural gas-fired steam generator were combined into a single data set, resulting in a total of seven data points. None of the units has air pollution control equipment. One of the units fired refinery process gas, while the other two fired natural gas. Thus, the composite emission factor and uncertainty incorporate these variations. The data set is normally distributed (Figure 3-1) and no data points were identified as outliers. Therefore, the arithmetic mean of the individual test run emission factors was taken to represent the central tendency of the results from these tests (Table 3-1). The average PM2.5 emission factor is 3.4×10^{-4} mg/dscm with an uncertainty of ±46 percent (at the 95 percent confidence level). The 95 percent confidence upper bound falls within the range of the data set.

Gas-Fired Process Heaters

Data from tests of three gas-fired process heaters were combined, providing nine data points in the data set (Table 3-2). Two of the units had no air pollution control equipment, while the third was equipped with SCR for NO_x control. Two units fired natural gas, while the other fired refinery process gas. The data are lognormally distributed (Figure 3-2) and no outliers were identified. Therefore, the arithmetic mean and uncertainty are conservative estimates of

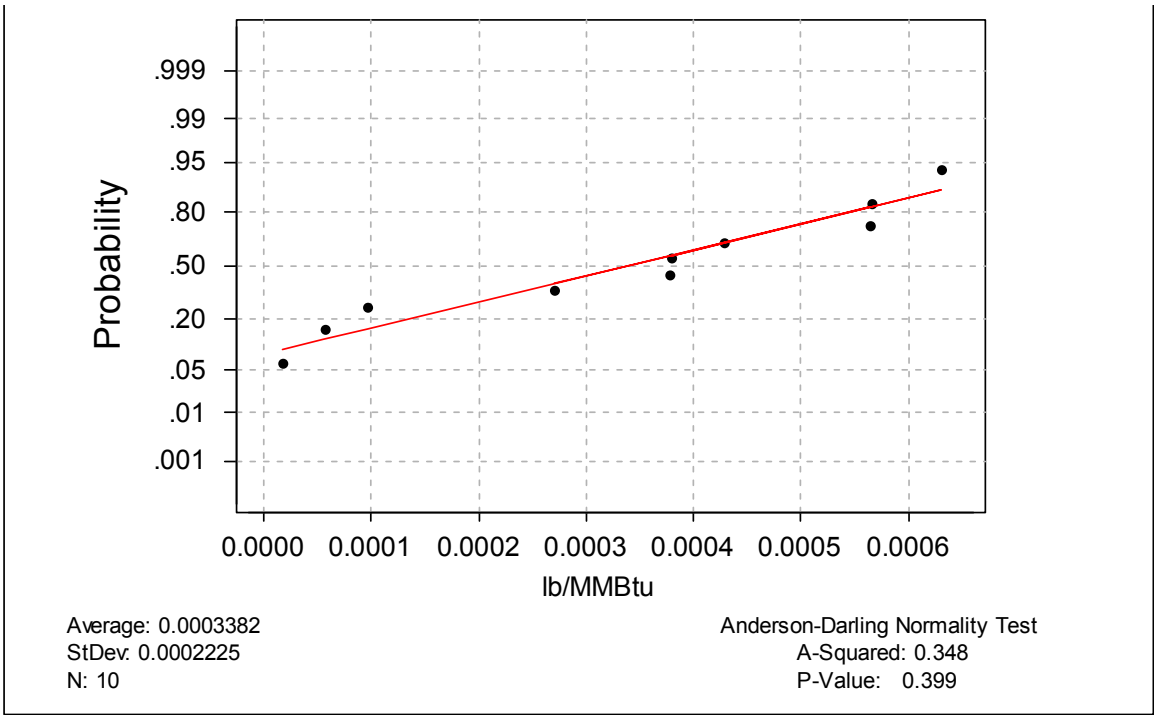
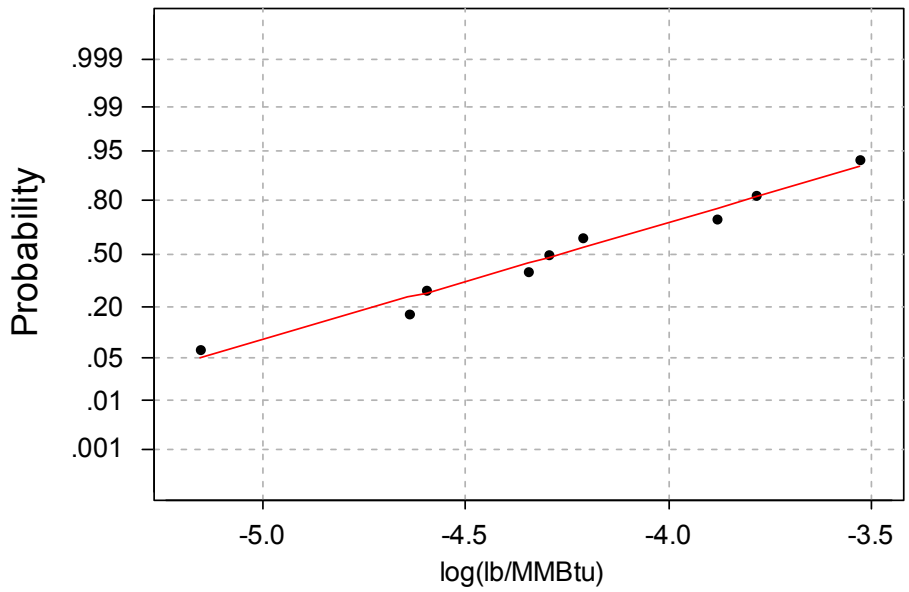


Figure 3-1. Normal Probability Chart for Gas-Fired Boiler PM2.5 Mass Results.

Table 3-1. PM2.5 Mass Emission Factors for Gas-Fired Boilers and Steam Generators.

Source	Description	Units	Value
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	1.7E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	5.6E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	9.6E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	2.7E-04
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	3.8E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	3.8E-04
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	4.3E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	5.6E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	5.7E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	6.3E-04
Average (mean)		**lb/MMBtu**	**3.4E-04**
Uncertainty (at 95% Confidence Level), %		%	46
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	4.7E-04
5th Percentile		lb/MMBtu	3.4E-05
95th Percentile		lb/MMBtu	6.0E-04



Average: -4.27187
StDev: 0.497745
N: 9

Anderson-Darling Normality Test
A-Squared: 0.170
P-Value: 0.901

Figure 3-2. Normal Probability Chart for Gas-Fired Process Heater PM2.5 Mass Results.

Table 3-2. PM2.5 Mass Emission Factor for Gas-Fired Process Heaters.

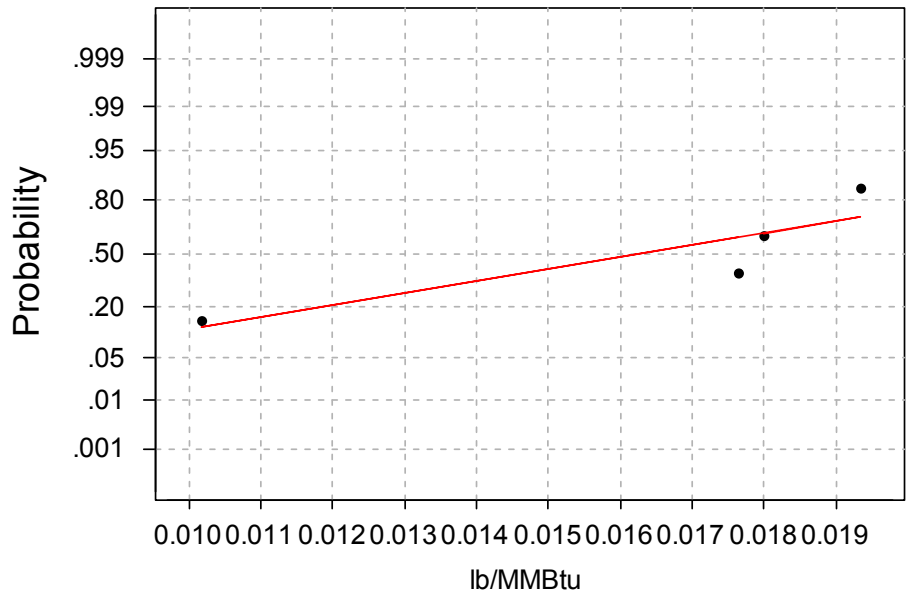
Source	Description	Units	Value
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	5.0E-05
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	6.1E-05
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	ND
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	4.5E-05
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	1.3E-04
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	2.3E-05
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	7.0E-06
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	1.6E-04
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	3.0E-04
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	NV
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	2.5E-05
Average		**lb/MMBtu**	**8.9E-05**
Uncertainty (at 95% Confidence Level), %		%	104
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	1.6E-04
5th Percentile		lb/MMBtu	1.3E-05
95th Percentile		lb/MMBtu	2.4E-04

emissions. The average emission factor is 8.9×10^{-5} with an uncertainty of ±104 percent at the 95 percent confidence level. The 95 percent confidence upper bound falls within the range of the data. The results from Site Charlie indicate it is likely that results are biased high due to

background PM2.5 in the dilution air. The results are not corrected for this bias since it is not known for every test run in the data set.

Oil-Fired Boilers

Only four data points from a single test form the data set for oil-fired institutional boilers. The data are normally distributed (Figure 3-3) and the lowest point tested as an outlier using the extreme value (Dixon's) test. No reason to exclude the data point was found. The average source-specific emission factor for the operating conditions of this test is 1.6×10^{-2} mg/dscm with an uncertainty of ±40 percent at the 95 percent confidence level (Table 3-3). The 95 percent upper confidence bound lies beyond the data range, a reflection of the small number of data points.



Average: 0.0162928
StDev: 0.0041429
N: 4

Anderson-Darling Normality Test
A-Squared: 0.533
P-Value: 0.065

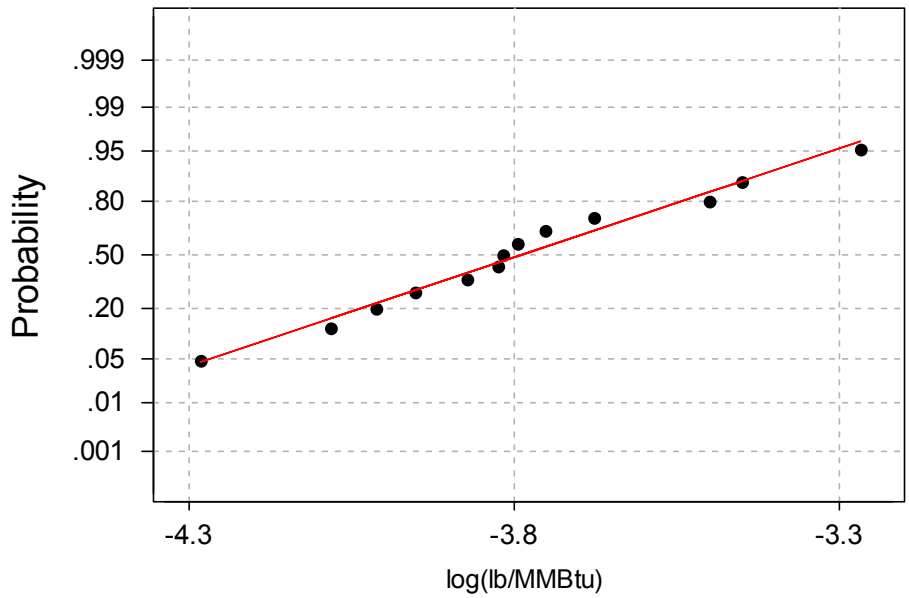
Figure 3-3. Normal Probability Chart for No. 6 Oil-Fired Institutional Boiler PM2.5 Mass Results.

Table 3-3. PM2.5 Mass Emission Factors for No. 6 Oil-Fired Institutional Boiler.

Source	Description	Units	Value
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	1.0E-02
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	1.8E-02
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	1.8E-02
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	1.9E-02
Average (log mean)		**lb/MMBtu**	**1.6E-02**
Uncertainty (at 95% Confidence Level), %		%	40
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	2.1E-02
5th Percentile		lb/MMBtu	1.1E-02
95th Percentile		lb/MMBtu	1.9E-02

Gas-Fired Internal Combustion Combined Cycle and Cogeneration Plants

Results of tests from two natural gas-fired combined cycle power plants and one refinery gas-fired cogeneration plant were combined for a total set of 13 data points. All of the units are equipped with similar post-combustion air pollution controls for NO_x and carbon monoxide (CO) emissions. Two of the units employ lean premix combustion systems, while the smaller unit (Site Golf) employed water injection for NO_x control. Two of the units were tested with duct burners (supplementary firing) operating during some or all of the test runs. Two units were fired on natural gas, while the other was fired on refinery process gas. The data from Site Echo include a total of seven data points, from tests at high load and low load. All seven points were included to provide a more robust indication of dispersion, although this biases the mean and uncertainty slightly. Results from Site Echo indicated that the results are probably positively biased due to background PM2.5 in the dilution air (England, 2004). The data are not corrected since a DSB was not collected for every run at every site. The data are lognormally distributed (Figure 3-4) and no outliers were identified. Therefore, the average and uncertainty are conservative estimates of PM2.5 emissions. The average PM2.5 emission factor is 1.9×10^{-4} with an uncertainty of ±49 percent at the 95 percent confidence level (Table 3-4). The 95 percent confidence upper bound falls within the data range. It should be noted that if background PM2.5 in the dilution air is subtracted from the stack PM2.5 for Site Echo, the corrected stack PM2.5 is indistinguishable from the measured ambient PM2.5 concentration at that site.



Average: -3.79238
StDev: 0.274355
N: 13

Anderson-Darling Normality Test
A-Squared: 0.197
-Value: 0.860

Figure 3-4. Normal Probability Chart for Gas-Fired Combined Cycle and Cogeneration Power Plant PM2.5 Mass Results.

Table 3-4. PM2.5 Mass Emission Factors for Gas-Fired Combined Cycle and Cogeneration Power Plants.

Source	Description	Units	Value
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (4)	lb/MMBtu	5.2E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	8.3E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	9.7E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.1E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.3E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.5E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.5E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.6E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.8E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	2.1E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	3.2E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	3.5E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	5.4E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	NV
Average		**lb/MMBtu**	**1.9E-04**
Uncertainty (at 95% Confidence Level), %		%	49
95% Confidence Upper Bound, lb/MMBtu (2)		lb/MMBtu	2.8E-04
5th Percentile		lb/MMBtu	7.0E-05
95th Percentile		lb/MMBtu	4.3E-04

(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% confidence upper bound provides a plausible upper bound (i.e., it is likely actual emissions are lower) for emissions.
(3) Duct burners on.
(4) Duct burners were on for a total of approx. 30 minutes of 360 minute run.
(5) High winds interfered with dilution sampler flow. Results biased high.

Diesel Engine

Tests at Site Foxtrot included tests of a Diesel-powered backup generator with and without a catalytic DPF at two different loads (50 and 75 percent of rated load). All measurements using

two different samplers for the DPF configuration are included (the result from each sampler was averaged for each test condition). Results for 50 and 75 percent load are combined for the base configuration but not for the DPF configuration because the combined data set is neither normal nor lognormal and the difference is significant at the 95 percent confidence level (based on t-test). The highest point in the 75 percent load DPF test is an outlier; however, no valid reason was found to exclude it. The average emission factor is 0.027 lb/MMBtu without the DPF and 0.0035 to 0.0046 with the DPF (Table 3-5).

Table 3-5. PM2.5 Emission Factors for a Diesel Engine.

Source	Description	Units	Value
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (50% load)	lb/MMBtu	2.6E-02
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (50% load)	lb/MMBtu	2.9E-02
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (50% load)	lb/MMBtu	2.9E-02
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (75% load)	lb/MMBtu	3.5E-02
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (75% load)	lb/MMBtu	2.1E-02
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine (75% load)	lb/MMBtu	2.4E-02
Average		**lb/MMBtu**	**2.7E-02**
Uncertainty (at 95% Confidence Level), %		%	35
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	3.5E-02
5th Percentile		lb/MMBtu	2.1E-02
95th Percentile		lb/MMBtu	3.4E-02

Source	Description	Units	Value
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.5E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.4E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.3E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.8E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.4E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (75% load)	lb/MMBtu	3.4E-03
Average		**lb/MMBtu**	**3.5E-03**
Uncertainty (at 95% Confidence Level), %		%	15
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	4.0E-03
5th Percentile		lb/MMBtu	3.3E-03
95th Percentile		lb/MMBtu	3.7E-03

Source	Description	Units	Value
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	4.7E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	4.6E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	4.7E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	4.0E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	4.8E-03
Site Foxtrot (Hernandez et al., 2004)	Diesel Engine with DPF (50% load)	lb/MMBtu	5.0E-03
Average		**lb/MMBtu**	**4.6E-03**
Uncertainty (at 95% Confidence Level), %		%	16
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	5.4E-03
5th Percentile		lb/MMBtu	4.2E-03
95th Percentile		lb/MMBtu	5.0E-03

PM2.5 PRECURSOR EMISSION FACTORS

Secondary PM2.5 is formed in the atmosphere by reactions involving precursor gases and sunlight to form ammonium nitrate, ammonium sulfate, and condensed organic aerosols. The most significant precursors are sulfur dioxide (SO_2), NO_x, ammonia (NH_3) and VOCs with a carbon number of eight and higher (VOC^{8+}). Only the reactions of VOC^{8+} are considered important in formation of secondary organic aerosols (Grosjean and Seinfeld, 1989), because the products from those having fewer than eight carbon atoms are too volatile to form aerosols under atmospheric conditions. The time scales of secondary aerosol formation are several hours to days after the exhaust enters the atmosphere, and controlling factors vary regionally. Therefore, it is appropriate to characterize emissions of the key precursors to facilitate analysis of impacts via air quality models.

PM2.5 precursor emission factors were developed in generally the same fashion as described above. VOC^{8+} results are based on Tenax sampling with the DRI dilution sampler for Sites A, B and C. Subsequent tests using both Tenax and canisters with the DRI dilution sampler at Sites Alpha, Bravo and Charlie generally showed the canister results to be more reliable. Therefore, the VOC^{8+} results for these sites and for Sites Echo and Golf are based on canister sampling with the DRI sampler. At two sites (Charlie and Echo), background levels in the dilution air were measured (see discussion in Section 2), and found to be significant relative to almost all VOC concentrations measured in the stack. For the majority of VOC^{8+}, the measured levels in the stack and ambient are were similar. Therefore, the results presented in this section are a conservative estimate of emissions, and quantification is highly uncertain. VOC^{8+} detected in at least two runs at each site are presented as the sum of all VOC^{8+} species, excluding certain compounds with large contributions but that are less than 10 times the higher of the DSB or the field blank. The reader is referred to the individual test reports for more details of the VOC^{8+} measurement methods and results.

In general, the SO_2 and NH_3 measurements were made using impregnated filters with the dilution sampler, except where noted. NO_x was measured with instrumental methods, typically either as part of a permanent monitoring system installed at the site or in a mobile laboratory. Precursor emission measurements were not made at Site Foxtrot because of the limited scope of that test's objectives.

Gas-Fired Boiler PM2.5 Precursors

NO_x data was obtained for all three gas-fired boilers, none of which was equipped with NO_x emission controls. Site Delta had significantly higher NO_x emissions than Sites A and C, most likely due to the older design of the institutional boiler at that site (Table 3-6). SO_2 emissions were measured at two sites, where very different levels were measured in the stack. This is because the refinery process gas at Site A had slightly elevated levels of sulfur (approximately 30 to 50 ppmw as elemental sulfur). Therefore, the emission factor for SO_2 is expressed as a linear correlation with fuel sulfur content (Figure 3-5). The fact that the constant is greater than zero implies either a low bias in the fuel sulfur measurement and/or a high bias in the stack measurement. NH_3 measurements were made at only one site, which is reflected in the high uncertainty associated with this result. VOC^{8+} results also have high uncertainty, a result of the slightly higher emission rate at Site Delta compared to Sites A and C.

Table 3-6. PM2.5 Precursor Emission Factors for Gas-Fired Boilers.

Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+}
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.059	n/a	n/a	4.7E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.062	na	na	6.3E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.057	n/a	n/a	1.1E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	3.5E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	1.9E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	2.3E-05
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0051	0.00061	1.8E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0020	0.0014	2.9E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0029	0.00083	1.4E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.19	ND	ND	1.0E-03
Average (mean)		**lb/MMBtu**	**0.11**	**2.9+1.8*ppmS**	**0.0009461**	**7.3E-04**
Uncertainty (at 95% Confidence Level), %		%	49	--	125	100
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.15	--	0.0018	8.3E-01
5th Percentile		lb/MMBtu	0.052	0.0022	0.00064	1.5E-05
95th Percentile		lb/MMBtu	0.18	0.012	0.0013	2.4E-03

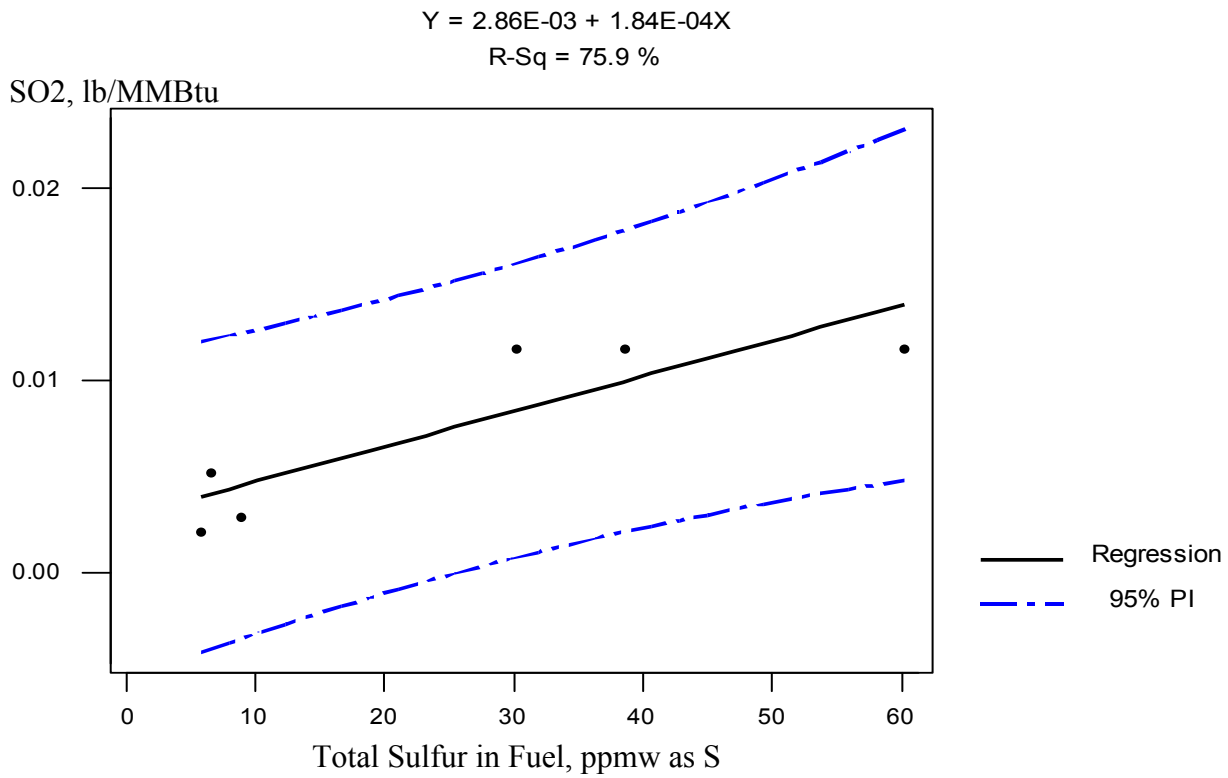


Figure 3-5. Correlation of SO_2 with Fuel Sulfur for Gas-Fired Boilers.

Gas-Fired Process Heater PM2.5 Precursors

NO_x and VOC^{8+} data were obtained at all three gas-fired process heater sites. Site Charlie had significantly lower NO_x emissions because it is equipped with SCR (Tables 3-7 and 3-8). Therefore, two emission factors were developed, one for the units without NO_x controls and one for Site Charlie. Because of the small populations within each subcategory, the uncertainty associated with these emission factors is large. Because of the small number of sources included in each category, the quality of the emission factors is not high.

At Site Charlie, measurements of dilution air background via a pre-test dilution system (dynamic) blank (DSB) showed that only three of 59 VOC^{8+} were present at more than 10 times the DSB, The average VOC^{8+} in-stack equivalent concentration was approximately 115 times the stack sample. Therefore, the VOC^{8+} results could be entirely due to background levels. Since the background level during actual stack tests was not determined, the background levels have not bee subtracted from the sample results. Further investigation of background levels is needed.

The significance of the DSB further emphasizes the need to use appropriate caution when applying the VOC^{8+} results.

Table 3-7. PM2.5 Precursor Emission Factors for Gas-Fired Process Heaters (without NOx Controls).

Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+} (1)
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	0.20	0.028	0.00025	0.00073
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	0.22	0.039	0.00024	0.00070
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	0.21	0.035	0.00034	0.0013
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	0.18	0.036	0.00019	0.00070
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	0.17	n/a	n/a	0.000007
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	0.17	n/a	n/a	0.000020
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	0.17	n/a	n/a	0.000027
Average (mean)		**lb/MMBtu**	**0.19**	**0.034**	**0.00025**	**0.00049**
Uncertainty (at 95% Confidence Level), %		%	23	104	88	95
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.23	0.032	0.00065	0.00087
5th Percentile		lb/MMBtu	0.17	0.029	0.00020	0.000011
95th Percentile		lb/MMBtu	0.22	0.039	0.00032	0.0011

(1) Site B based on Tenax results. Site Alpha based on canister results. Results likely biased high due to dilution air background.

Table 3-8. PM2.5 Precursor Emission Factors for Gas-Fired Process Heaters (with NOx Controls).

Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+} (1)
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.013	0.00063	0.00045	0.00092
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.015	0.00049	0.00096	0.0011
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.015	0.00025	0.00035	0.00052
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.014	0.00024	0.00026	0.00041
Average (mean)		**lb/MMBtu**	**0.014**	**0.00040**	**0.00051**	**0.00074**
Uncertainty (at 95% Confidence Level), %		%	18	104	88	76
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.17	0.032	0.00065	0.0012
5th Percentile		lb/MMBtu	0.013	0.00024	0.00028	0.00042
95th Percentile		lb/MMBtu	0.015	0.00061	0.00089	0.0011

(1) Based on canister results. Results likely biased high due to dilution air background.

Combined Cycle/Cogeneration Unit PM2.5 Precursors

Data from the three gas-fired combined cycle/cogeneration units tested in this program provide 11 to 14 data points for PM2.5 precursor emissions (Table 3-9). All of the units have NO_x and CO emission controls, and tests at Site Bravo included tests with duct burners operating in the heat recovery steam generators (supplementary firing). Site Golf differs significantly in size (smaller) and design compared to Sites Bravo and Echo. SO_2 and VOC were not measured at Site Golf. The data sets are slightly biased towards the Site Echo results because all seven test runs (four runs at high load and three runs at reduced load) are included. In addition, operating conditions varied significantly among the four test runs at Site Bravo. The population of data is

Table 3-9. PM2.5 Precursor Emission Factors for Gas-Fired Internal Combustion Combined Cycle/Cogeneration Plants (with NOx and CO Controls).

Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+}
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0089	0.00098	0.0015	0.0013
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0081	0.0012	0.0015	0.00084
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (4)	lb/MMBtu	0.0056	0.00072	0.0018	0.00074
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0035	0.00010	0.0015	0.00079
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0072	0.00021	0.014	0.00072
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0085	0.00027	0.0044	0.00034
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0082	0.00040	0.0024	0.00042
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0077	0.00051	0.0025	0.00023
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0079	0.00030	0.0044	0.00026
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0083	0.00040	0.0068	0.00026
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0080	0.00041	0.0056	0.00041
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0059	n/a	0.0070	n/a
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0060	n/a	0.0063	n/a
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0063	n/a	0.0058	n/a
Average (mean)		**lb/MMBtu**	**0.0072**	**0.00050**	**0.0047**	**0.00058**
Uncertainty (at 95% Confidence Level), %		%	24	55	30	54
95% Confidence Upper Bound, lb/MMBtu (2)		lb/MMBtu	0.0087	0.00073	0.0059	0.00085
5th Percentile		lb/MMBtu	0.0049	0.00016	0.0015	0.00025
95th Percentile		lb/MMBtu	0.0086	0.0011	0.0096	0.0011

(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t
(3) Duct burners on.
(4) Duct burners were on for a total of approx. 30 minutes of 360 minute run.
(5) High winds interfered with dilution sampler flow. SO2, NH3 and VOC8+ results biased high.

still considered small. As noted earlier, emission factors derived from tests of these three units do not represent the source tested, the entire population of such units or any particular operating conditions, but are simply the average of emissions measured under the operating conditions during these tests.

DSB results at Site Echo indicate it is likely that background levels in the dilution air are significant relative to those in the stack samples for most of the VOC^{8+}. Most or all of the

reported results may be due to this background; therefore, the reported VOC8+ emission factor is a very conservative estimate of emissions (see discussion of Site Echo results in Section 2). Further investigation of dilution air background levels and their significance to stack results is needed. The reader is referred to the individual test reports for further details of the test methods and results.

Oil-Fired Boiler PM2.5 Precursors

Only four data points from a single unit comprise the data set for oil-fired boilers (Table 3-10). SO_2 results are based on measurements using iced impinger methods (not dilution). The uncertainty of the VOC8+ results is greater than 100 percent, indicating the results cannot be distinguished from zero of the MDL at the 95 percent confidence level.

Table 3-10. PM2.5 Precursor Emission Factors for No. 6 Oil-Fired Boiler.

Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+}
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	0.36	NV	1.2E-05	0.00072
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	0.32	NV	6.7E-06	0.00095
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	0.39	NV	7.1E-06	0.0011
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (No. 6 Oil)	lb/MMBtu	0.40	NV	9.0E-06	0.0034
Average (mean)		**lb/MMBtu**	**0.37**	**NV**	**8.7E-06**	**0.0016**
Uncertainty (at 95% Confidence Level), %		%	20	NV	95	123
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.43	NV	1.7E-05	0.0030
5th Percentile		lb/MMBtu	0.32	NV	6.8E-06	0.00076
95th Percentile		lb/MMBtu	0.40	NV	1.1E-05	0.0031

NV - test results not valid.

PM2.5 SPECIATION PROFILES

Speciation profiles for PM provide a means of estimating the emissions of PM species based on a measurement or emission factor for total PM emissions. One of the principal applications of speciation profiles is for source-receptor and source apportionment models, such as CMB8 (Watson et al., 1997). Receptor models require profiles that express the speciated substance abundances in terms of the mass fraction of the substance in the total emissions stream and the uncertainty associated with that mass fraction. Speciated PM emission factors also are useful for estimating impacts of PM species emissions on air quality, e.g., atmospheric visibility (Ryan, 2002). EPA's SPECIATE database contains one of the largest compilations of speciation profiles (U.S. EPA, 2002b). Many of the profiles currently in SPECIATE are drawn from results generated in the 1980's and in some cases the 1970's and it is debatable whether these represent

current source emissions. For example, prior to the 1999 update, the PM profile for natural gas-fired combustion turbines was based on results of a poorly documented jet engine test; this profile was removed in the 1999 update with no data to replace it. Due to the pending implementation of the PM2.5 NAAQS, EPA added 13 new PM profiles (some replaced older profiles) to SPECIATE in 1999 (U.S. EPA, 2002c), and is currently seeking to identify new profiles for eventual inclusion in a future update (Hodan, 2002). It is expected that a significant number of new profiles will be added to SPECIATE because of this research. Most of the new profiles in SPECIATE will be drawn from articles published in peer-reviewed journals. EPA has not developed a formal procedures manual or acceptance criteria for preparing speciation profiles, however EPA has provided reviews of 178 articles published between 1990 and 2002 that provides insight into their process (Hodan, 2002).

EPA convened an expert panel of potential SPECIATE users and data suppliers in October 2002 to re-evaluate speciation needs (Hodan, 2002). Members of that group recommended that no hot stack samples or hot filter/iced impinger results should be used for PM speciation profiles because they do not represent actual condensed particle emissions (Watson and Chow, 2002). It was recommended that PM speciation profiles include, as a minimum, major elements (at least those reported by the IMPROVE and PM2.5 Speciation Trends networks), major water-soluble ions – $SO_4^{=}$ and nitrate ion (NO_3^-) at a minimum, preferably also NH_4^+, potassium, sodium, chloride, fluoride, phosphate, calcium, and magnesium ions), and carbon fractions (total carbon (TC), OC, and EC, preferably with other fractions that are defined by the method such as the eight IMPROVE fractions, and carbonate carbon); organic fractions, isotopic abundances, organic compounds, and single particle properties should be included where they are well-defined, and can be normalized to PM or organic mass. The speciation profiles reported here are intended to be consistent with these recommendations.

Speciation profiles and their related uncertainty were recalculated for each source using data from the original test reports, since conventions for calculating profiles varied among the different reports. At the low PM2.5 mass concentrations for these sources, the effects of OC measurement artifacts (adsorption of gaseous VOC on the QFFs) becomes apparent as the sum of species typically exceeds the measured PM2.5 mass by 50 percent or more (accounting for oxidation states and OC species). Therefore, the profiles were normalized to the sum of species.

The sum of species and mass fraction of individual species were calculated for each test run. The average mass fraction and uncertainty were then calculated for all runs at each source. The recalculated profiles include only species detected in at least two runs at each site; undetected results were treated as zeros in calculating the average mass fraction and uncertainty so that the sum of the average mass fractions equals zero. The highest stable oxide form was assumed for elements, and OC was multiplied by a factor of approximately 1.08[2] to account for hydrogen and heteroatoms in the OC species (based on the measured SVOC composition). The source profiles for each test run within a source category were combined as the arithmetic mean to represent average emissions compositions for a source category. Detailed data are available in the individual test reports listed at the end of Section 1 for compositing profiles based on other criteria.

It is likely that a significant degree of bias exists in the source profiles for gas-fired sources due to background levels in the dilution air. Results from Site Echo and Site Charlie indicate that the background levels of most species can be very significant relative to their respective concentrations in the stack of gas-fired sources. This is a reflection of the extremely low concentrations of species in the exhaust of the gas-fired sources. See Section 2 for additional discussion of dilution air background. Since dilution air background was not determined for all test runs in the data set, the level of background is unknown for most of the tests. In addition, the test results indicate it is likely that the OC fraction, which comprises the dominant fraction of species for gas-fired sources, is positively biased due to organic vapor adsorption artifacts (see Section 2 for further discussion). Because of these factors, the results represent conservative estimates of emissions. Therefore, it is very important that the results for the gas-fired units should be applied with appropriate caution.

All of the PM2.5 speciation profiles presented below are based on dilution sampling results. Tests at Sites Alpha, Bravo and Charlie, in which side-by-side measurements were made with

[2] Note, this correction factor assumes that most of the OC consists of species similar to those quantified in the SVOC analysis (which was limited to polycyclic aromatic hydrocarbons). Since only a very small fraction of the total OC is represented by the measured species, this correction may not reflect the actual OC composition. For ambient air samples, the correction is generally larger, typically on the order of 1.4 or more. In most cases, the sum of species using 1.08 as a correction factor exceeded the PM2.5 mass measured gravimetrically, and a higher correction factor would further increase the imbalance. This lends further evidence of the likelihood of positive bias in the OC results due to the VOC adsorption artifact.

traditional hot filter/iced impinger methods and dilution sampling, indicate that both mass and speciation are highly method dependent. Therefore, these PM2.5 speciation profiles should be used only with PM2.5 mass results based on dilution sampling, otherwise large errors are likely.

Gas-Fired Boiler PM2.5 Speciation Profile

Individual PM2.5 speciation profiles from each test run on all three boilers/steam generators were combined into a single profile. The PM2.5 speciation profile for gas-fired boilers is dominated by carbon, with an average of 61 percent OC and 13 percent EC (Table 3-11). It is likely that the carbon results are biased high due to OC measurement artifacts associated with VOC adsorption on the samples and quartz filters, and EC results are dominated by Site A tests during which the boiler operated at low load and with visibly sooty (yellow) flames. Backup OC (58 percent mass fraction) indicates the potential magnitude of the OC artifact is nearly the same as the measured stack results (61 percent mass fraction). The sum of species generally exceeded the measured PM2.5 mass by approximately 50 to a few hundred percent, which provides further indication that the carbon results may be biased. See discussion of OC/EC measurements in Section 2 for further details. $SO_4^=$ is the next most significant fraction (6.9 percent mass fraction) after carbon. Uncertainty of the remaining mass fractions is greater than 100 percent, which indicates they were detected but are not quantifiable with at least 95 percent confidence.

Gas-Fired Heater Speciation Profile

The PM2.5 speciation profiles from all runs on the three gas-fired process heaters were combined into a single profile. OC is the predominant PM2.5 component (62 percent mass fraction), followed by $SO_4^=$, EC, ammonium ion (NH_4^+) and lesser fractions of other ions and elements (Table 3-12). Backup OC results also show it is likely that there is significant positive bias in the OC mass fraction.

Gas-Fired Internal Combustion Combined Cycle/Cogeneration Plant Speciation Profile

The individual speciation profiles from each test run of the three units tests were combined into a single composite. At Site Echo, side-by-side measurements with the DRI and compact samplers were performed. The results from the two samplers were averaged for each test run, and the

Table 3-11. PM2.5 Speciation Profile for Gas-Fired Boilers.

	Average Mass Fraction, % (1)	Uncertainty, relative % (95% Confidence)	95% Confidence Upper Bound, %	Number of Runs
OC (2)	61	37	81	10
EC	13	82	22	10
SO4=	6.9	96	13	10
Cu	0.5	71	0.8	10
Si	5.8	175	15	10
Ca	4.0	237	13	10
Fe	2.2	139	4.9	10
NH4+	1.6	123	3.3	10
Al	1.2	135	2.8	10
K	1.0	193	2.7	10
NO3-	0.9	119	1.8	10
Zn	0.8	229	2.5	10
Ni	0.5	233	1.5	10
Cl-	0.3	261	0.9	10
V	0.2	220	0.5	10
Ti	0.1	503	0.6	10
Mn	0.1	143	0.2	10
As	0.04	119	0.1	10
Co	0.04	225	0.1	10
P	0.03	1012	0.4	10
Pb	0.03	276	0.1	10
Br	0.02	238	0.1	10
Sr	0.01	289	0.1	10
Cr	0.01	773	0.1	10
Backup OC (2)	58	21	67	3

Shaded area represents uncertainty greater than 100 percent. Results may not be suitable for quantitative analysis. Presented for information only.

(1) Normalized by sum of species.

(2) Backup OC indicates a significant potential positive bias in OC measurement. See text.

Table 3-12. PM2.5 Speciation Profile for Gas-Fired Process Heaters.

	Average Mass Fraction, % (1)	Uncertainty, relative % (95% Confidence)	95% Confidence Upper Bound, %	Number of Runs
OC (2)	62	20	72	11
SO4=	11	64	16	11
EC	6.3	64	9.7	11
NH4+	3.7	88	6.3	11
Si	3.5	67	5.4	11
NO3-	2.5	66	3.8	11
Fe	2.5	87	4.2	11
Ca	1.9	66	3.0	11
Al	1.3	63	2.0	11
Cu	1.0	99	1.8	11
K	0.5	72	0.8	11
Ni	0.06	83	0.1	11
Zn	1.4	105	2.5	11
Co	1.1	207	2.9	11
Cl-	1.0	101	1.8	11
Ba	0.4	300	1.4	11
P	0.1	139	0.3	11
Ti	0.08	647	0.6	11
Cd	0.05	315	0.2	11
Cr	0.04	169	0.1	11
Mn	0.04	148	0.09	11
V	0.02	1218	0.2	11
Pb	0.01	566	0.09	11
Br	0.01	295	0.03	11
Sr	0.01	720	0.05	11
Zr	0.004	746	0.03	11
Backup OC (2)	58	33	73	8

Shaded area represents uncertainty greater than 100 percent. Results may not be suitable for quantitative analysis. Presented for information only.

(1) Normalized by sum of species.

(2) Backup OC indicates a significant potential positive bias in OC measurement. See text.

analytical and sampling uncertainties were combined by addition in quadrature. The results for each run were then combined with the runs from the other sites using similar procedures. As noted earlier, the composite speciation profile does not represent the individual source tested, all units within the source category or any particular operating condition due to the limited size of the data set and variations in design and operation among the units tested.

The composite speciation profile is similar in character to the other gas-fired units, with OC being the dominant constituent followed by $SO_4^{=}$, NH_4^{+} and lesser amounts of other ions and

elements (Table 3-13). Backup OC indicates there may be a significant positive bias in the OC results.

Oil-Fired Boiler Speciation Profile

Only four data points from a test of one unit comprise the No. 6 oil-fired boiler speciation data set. The PM2.5 mass is dominated by $SO_4^=$ (60 percent mass fraction), which is expected based on the elevated fuel sulfur and ash content compared to gas fuels (Table 3-14). OC, EC, nickel (Ni), silicon (Si), NH4+ and lesser amounts of other elements comprise the balance of the profile. The elemental composition reflects several probable constituents of the No. 6 oil ash (e.g., Si, Ni, vanadium (V)). The generally low uncertainties for each mass fraction, compared to the gas-fired units, reflect the much larger mass of PM2.5 collected from these tests and homogenous ash composition of the fuel.

Diesel Engine Speciation Profile

The speciation profile is derived entirely from Site Foxtrot test results. The only species measured were EC, OC, and ions. The sum of species agreed fairly well with the measured PM2.5 mass, so these species capture the major features of the profile. Profiles were derived separately for the base (no emission controls and sulfur content typical of California Diesel fuel specification) and DPF (with ultra-low sulfur Diesel fuel) configurations. EC and OC dominate the speciation profile (Table 3-15) for both the base (78 percent and 22 percent mass fractions, respectively) and DPF (83 and 16 percent mass fractions, respectively). The base test runs were significantly shorter (typically 20 minutes) than the DPF test runs (typically 2 hours) because of the higher PM concentration in the base configuration. As a result, some species were detected in the DPF configuration tests were undetectable during the base configuration tests. This may explain the absence of NO_3^- and $SO_4^=$ in the base configuration profiles. Elevated NO_3^- concentrations also could be expected in the DPF configuration since the DPF creates it as an intermediate part of the process.

Table 3-13. PM2.5 Speciation Profile for Gas-Fired Internal Combustion Combined Cycle/Cogeneration Plants with Air Pollution Control Equipment.

	Average Mass Fraction, % (1)	Uncertainty, relative % (95% Confidence)	95% Confidence Upper Bound, % (2)	Number of Runs
OC (2)	68	16	78	13
SO4=	13	43	18	13
NH4+	6.0	40	8.0	13
Cl-	3.0	51	4.4	13
NO3-	2.7	53	4.0	13
EC	2.5	79	4.2	13
Si	1.8	65	2.8	13
Fe	0.9	100	1.6	13
Ca	0.4	81	0.7	13
Al	0.4	86	0.6	13
K	0.3	44	0.5	13
Zn	0.1	82	0.2	13
Br	0.03	76	0.1	13
Cu	0.1	116	0.1	13
Ti	0.03	923	0.4	13
Ni	0.03	122	0.1	13
Mn	0.02	159	0.05	13
V	0.01	1114	0.2	13
Mo	0.01	276	0.03	13
Pb	0.01	359	0.03	13
Co	0.004	387	0.02	13
Backup OC (3)	66	22	78	13

Shaded area represents uncertainty greater than 100 percent. Results may not be suitable for quantitative analysis. Presented for information only.

(1) Normalized by sum of species. Includes data from units of different size, configuration, air pollution controls, load and duct burners on/off. High winds interfered with dilution flow measurements on two tests, those results may be biased slightly high. See footnotes on Table 3-9.
(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% confidence upper bound provides a plausible upper bound (i.e., it is likely actual emissions are lower) for emissions.
(3) Backup OC indicates a significant potential positive bias in OC measurement. See text.

Table 3-14. PM2.5 Speciation Profile for No. 6 Oil-Fired Institutional Boiler.

	Average Mass Fraction, % (1)	Uncertainty, relative % (95% Confidence)	95% Confidence Upper Bound, %	Number of Runs
SO4=	60	24	71	4
OC (2)	7.9	46	11	4
EC	7.1	94	12	4
Ni	4.7	25	5.7	4
Si	4.6	28	5.6	4
NH4+	3.3	23	3.9	4
Ca	2.8	28	3.4	4
Zn	2.7	35	3.4	4
Fe	2.3	23	2.8	4
Al	1.5	37	1.9	4
V	1.0	33	1.3	4
P	0.37	88	0.63	4
K	0.32	31	0.40	4
Co	0.29	24	0.34	4
Sb	0.19	26	0.23	4
La	0.19	32	0.24	4
Cl-	0.16	26	0.20	4
Cu	0.14	32	0.18	4
Ti	0.12	27	0.14	4
Pb	0.11	36	0.14	4
Mo	0.079	33	0.10	4
Ba	0.058	38	0.076	4
Cr	0.049	37	0.065	4
Mn	0.039	24	0.046	4
Sn	0.034	35	0.043	4
Sr	0.015	22	0.017	4
Ga	0.011	52	0.015	4
Zr	0.0034	39	0.0045	4
As	0.013	190	0.038	4
Tl	0.0015	230	0.0049	4
Y	0.0013	110	0.0024	4
Backup OC (2)	1.4	66	2.1	4

Shaded area represents uncertainty greater than 100 percent. Results may not be suitable for quantitative analysis. Presented for information only.

(1) Normalized by sum of species.

(2) Backup OC indicates a significant potential positive bias in OC measurement. See text. Result not included in sum of species.

Table 3-15. PM2.5 Speciation Profile for Diesel Engine.

	Average Mass Fraction, % (1)	Uncertainty, relative % (95% Confidence)	95% Confidence Upper Bound, %	Number of Runs
Base (uncontrolled):				
EC	78	4	81	6
OC (2)	22	12	24	6
Backup OC (2)	10	22	12	6
DPF				
EC	83	6	86	6
OC (2)	16	27	19	6
NO3-	1.6	17	1.8	6
SO4=	0.3	131	0.6	6
Backup OC (2)	6.2	34	8.1	6

Shaded area represents uncertainty greater than 100 percent. Results may not be suitable for quantitative analysis. Presented for information only.

(1) Normalized by sum of species.

(2) Backup OC indicates a significant potential positive bias in OC measurement. See text.

4. FINDINGS AND RECOMMENDATIONS

PM2.5 EMISSION CHARACTERISTICS

The focus of this program was to develop and apply dilution sampling for gas- and oil-fired stationary combustion sources to characterize PM2.5 mass, PM2.5 species and gaseous PM2.5 precursor emissions. These kinds of data are needed for PM2.5 source apportionment and other air-quality analyses that will be conducted as part of implementing the PM2.5 NAAQS over the next several years. The work was conducted because the few existing data do not represent emissions from current-day sources and/or are based on methods that are outdated or have known problems, especially for gas-fired sources. Gas combustion is a major energy source for the petroleum industry and other industrial sources that is expected to increase in use dramatically over the next 20 years. In addition, oil combustion continues to be both a major product for the petroleum industry and a common end user fuel for point and area sources in urban areas exceeding ambient air PM2.5 standards. Comparative tests using both traditional hot filter/iced impinger methods and dilution sampling previously showed that traditional methods overestimate PM2.5 and species emissions from gas combustion, typically by more a factor of 10 or more. Therefore, this program filled a need to advance dilution sampling methods and gather data for these kinds of sources.

The reader is directed to the individual reports listed at the end of Section 1 for details of the project findings. The overall key findings related to PM2.5 emission characteristics of the various sources tested in this project are:

- PM2.5 Mass. For gas-fired sources, dilution sampling indicates PM2.5 mass emissions are extremely low -- probably near ambient air PM2.5 concentrations in many cases. Such levels are difficult to quantify with high confidence using any of the test methods applied in this program – far below both the estimated MDL and LQL of traditional hot filter/iced impinger methods, and generally between the estimated MDL and LQL of the dilution sampling method. Traditional methods for measuring filterable and condensable PM previously have been shown to be subject to small systematic and random biases (due to sampling artifacts and biases) that are very significant at the extremely low PM concentrations typical of gas-fired sources. The in-stack PM2.5 MDL and LQL achieved with dilution sampling are far lower than can be achieved by traditional hot filter/iced impinger methods due to the avoidance of such biases and greater analytical sensitivity. Therefore, the PM2.5 concentration in stack gases from gas-fired sources measured using

dilution sampling is far lower than that measured by traditional methods. While a degree of systematic and random bias in the dilution sampling measurements remains (primarily due to background PM2.5 in the dilution air), these results for gas-fired sources are considered more representative of actual emissions. PM2.5 mass emissions from No. 6 oil-fired sources and Diesel engines are well above the MDL and LQL of the dilution sampling method. Further work on the dilution sampling method is needed, especially for gas-fired source applications, as further discussed below.

- PM2.5 Speciation. The reconstructed PM2.5 mass (sum of species adjusted for element oxides and OC speciation) for gas-fired sources was typically greater than the measured PM2.5 mass by 25 to as much as 200 percent or more in some cases. For the oil-fired boiler and the Diesel engine, the reconstructed and measured PM2.5 mass are in good agreement (within approximately 10 percent). This implies a significant degree of positive bias in the PM2.5 species measurements for the gas-fired sources. For gas-fired sources, dilution sampling results indicate that the majority of PM2.5 is OC (as defined by the thermal-optical reflectance analytical method using the IMPROVE protocol). However, quality assurance measurements indicate it is likely that the OC fraction is overestimated due to adsorption of VOC on the sample and quartz filters. This probably explains the imbalance between actual and reconstructed mass. Because of this imbalance, the speciation profiles are normalized to the reconstructed mass rather than the measured mass.

  Measured SVOC species typically accounted for much less than 5 percent of the OC mass. This indicates the likelihood of either a positive bias in the OC measurement and/or the presence of other organic compounds such as fuel fragments and combustion intermediates that were not quantified. In this test program, the SVOC analysis method was optimized for quantification of polycyclic aromatic hydrocarbons (PAH) commensurate with the test objectives. The results strongly suggest that most of the OC mass is accounted for by species other than PAH. A modified analytical approach is recommended in future tests if the objective is to fully speciate the OC mass.

  The PM2.5 speciation profiles for gas-fired sources are not distinctive for source apportionment purposes due to the predominance of OC and high uncertainty resulting from the extremely low concentrations of individual species. $SO_4^{=}$, EC, NH_4^+ and other ions and elements are minor components for gas-fired sources. $SO_4^{=}$ is the dominant PM2.5 species for the oil-fired boiler, while EC dominates for the Diesel engine. The speciation profile for the oil-fired boiler also showed elements consistent with the ash content of the fuel that may provide a distinctive signature.

- Particle Size. The test results for gas-fired units indicate that substantially all of the PM in the stack was smaller than 2.5 micrometers. In-stack cyclones with 10 and 2.5 µm cutpoints were used in most tests; however, the results are generally below the MDL of the acetone rinse procedure used to recover PM collected in the cyclones. Recovery of the internal PM2.5 cyclone in the dilution sampler also did not reveal any detectable deposits of larger particles. Exploratory ultrafine (0.1 µm and smaller) particle

measurements revealed that peak number concentrations occurred at a size of approximately 20 nm, indicating the predominance of particles formed by nucleation, and that ultrafine particles accounted for approximately one-third of the total PM2.5 mass, assuming unit density (1 g/cc) for ultrafine particles.

Particle size and composition measurements for the No. 6 oil-fired boiler test showed that approximately 76 percent of the particle mass is represented by particles smaller than 0.32 μm and that the majority of these are $SO_4^=$ related. This is reasonable considering the elevated sulfur content of the fuel compared to the other sources tested in this program.

Diesel engine test results with and without a DPF show ultrafine particle number concentration peaks at 60 to 80 nm and that both total and ultrafine particles were significantly reduced by the DPF. Although some studies by others have suggested that addition of a DPF may increase the number of ultrafine particles in Diesel engine exhaust, this was not observed in these tests. The long residence times characteristic of the dilution samplers used in this study may account for at least part of this difference, since the lifetime of ultrafine particles is generally short due to rapid accumulation.

DILUTION METHOD READINESS

Equipment

Prior to this program, most recent (since about 1990) stationary source dilution sampling tests employed the large dilution sampler developed by Hildemann et al. (1989) at CalTech, primarily as part of research projects focused on PM2.5 source apportionment. This system became the benchmark because it is very well characterized in the literature and because it was designed specifically for characterizing organic aerosols (of special interest for source "fingerprinting"). A derivative of this design from DRI was used for five of the six sources tested in this program. While this dilution sampler was used successfully in this and other projects and still serves as an excellent research tool, it is impractical for widespread routine testing because its large size and weight precludes its use at many sampling locations. A compact dilution sampler was designed and tested in this program in recognition of the need for improved source emissions data for implementing the PM2.5 NAAQS. The prototype sampler was used successfully in tandem with the DRI sampler at two sources and alone at a third source. The key findings with respect to the new compact sampler are:

- Systematic and Random Variation (Accuracy and Precision). Tests comparing the compact sampler to an existing benchmark dilution sampler showed that the two samplers yield results that are the same at the 95 percent confidence level. However, further testing is needed to better quantify systematic and random variation, especially for applications with extremely low (less than approximately 1 to 2 mg/dscm) PM concentrations. Measurement background levels in the dilution air were found to be significant in some tests relative to stack concentrations for gas-fired sources, indicating the potential for further improvements in the equipment and/or procedures to reduce systematic variation for this application.

- Physical Size and Weight. For determining PM2.5 mass, elements, ions, and OC/EC, the prototype compact sampler and ancillary equipment are in total approximately the same physical size and weight as traditional particulate sampling equipment. Adding speciation modules and instrumentation increases the overall size and weight, but to a lesser extent than the equivalent equipment that would be required to obtain a similar scope of speciation using traditional methods.

- Operation. For this program, the sampler was instrumented and equipped with an off-the-shelf computer data acquisition system. Adjustments to the system were made manually. With further engineering of the instrumentation, software and controls, it should be feasible to simplify operation such that it can be operated by a qualified source test individual.

- Sample Recovery. The loading and recovery of sample filter media using ambient air sampling equipment is significantly less complex than traditional hot filter/iced impinger method equipment, with much less potential for contamination and sample loss in the field. The compact sampler design makes it much easier to clean and recover samples from the interior surfaces compared to the benchmark dilution sampler. However, the acetone rinse procedure used to recover deposits from the probe and sample venturi (adopted from EPA Method 5) lacks sufficient sensitivity for applications with extremely low PM concentration. Other studies imply that PM2.5 deposits in the probe and sample venturi are negligible, therefore the acetone rinse results were ignored for tests of gas-fired sources.

Equipment ruggedness was not evaluated during this program but is an important consideration for commercial applications. Further engineering of the mechanical design is needed for commercial application. It is expected that commercial equipment makers will be able to take the design criteria developed in this program and develop commercial designs that are sufficiently rugged for routine stack testing purposes.

Procedures and Methodology

Detailed operating procedures evolved during the course of the program as weaknesses and problems were identified. These are summarized in Section 2 and in a companion report (England and McGrath, 2004). At this stage, procedures are adequate for achieving the levels of method performance reached in this program. These are generally adequate for research purposes. Further definition of routine QA/QC activities (e.g., DSBs and other blanks) is needed.

Recovery of deposits from the sample probe and venturi was shown to be important for sources with high PM loading. Traditional procedures based on EPA Method 5 (U.S. EPA, 1996a) were used. These procedures were shown to be problematic for gas-fired sources due to background levels in the reagent (acetone) and variability of the analytical procedure. As a result, all results for gas-fired sources were below the MDL and/or LQL of the procedure. This problem is not unique to dilution sampling but also applies equally to EPA Method 5. EPA estimates that a minimum catch of 7800 µg is needed for the acetone rinse for 99 percent confidence that all results will be within 10 percent tolerance (Shigehara, 1996). This falls far short of the needs for characterizing gas-fired sources, where typical acetone rinse weights of 500 to 2000 µg in the blanks were found (reagent blanks were within EPA Method 5 specifications). An improved or alternative procedure is needed for gas-fired and other low concentration sources.

Data Quality

Data quality is measured primarily by MDL and LQL, which characterize random variation (measurement noise or precision), and blanks, which characterize potential systematic variation (bias or accuracy). During these tests, preliminary estimates of random and systematic variation were made based on overall test results and comparison tests. The uncertainty of each measurement was presented for each result and preliminary estimate of MDL and LQL was developed. Field blanks and trip blanks generally showed insignificant background levels in the reagents and sample collection media, and lack of contamination in the field or laboratory. Dilution system (dynamic) blanks showed that background levels in the dilution air can be significant for gas-fired sources, which detracts from the overall quality of the data for these sources. The DSB levels are not significant for the Diesel engine and oil-fired boiler tests. The

results indicate the need for further investigation to determine whether dilution air background levels can be reduced and/or measured with sufficient reliability to correct the sample results.

RECOMMENDATIONS FOR FUTURE WORK

Although significant advancements were achieved in both the technology of dilution sampling and source emissions characterization, the results indicated the need for further work in the areas listed below.

Dilution Method Improvements and Validation:

Recommendations to address dilution air background, recovery of and to better quantify MDL and PQL are:

- Dilution Air Improvements. Purified ambient air currently is used for dilution. The current system utilizes HEPA and activated carbon filters to remove particles and organic compounds from the ambient air. Nevertheless, background levels of particles and organic compounds in the dilution air frequently proved to be significant for tests of gas-fired sources. Means to reduce background levels in the dilution air should be investigated for gas-fired sources. The removal efficiency and cost-effectiveness of other technologies such as ultra-low penetrating air (ULPA) filters, electrostatic precipitation, condensing heat exchangers, and other technologies should be explored to reduce breakthrough of fine and ultrafine particles. Alternatively, pure compressed gases (e.g., Battelle, 1994) instead of purified ambient air may be necessary for some applications. If reduction of background levels is not feasible, procedures to correct for the background levels should be implemented. For example, DSBs could be collected for every test run, using either integrated or an instrumental methods (e.g. SMPS or laser photometer), and the results used to correct the stack sample results.

- Probe Recovery Procedures. The acetone rinse recovery and analysis procedure, used to recover and quantify deposits from the sample probe and venturi, needs to be improved or replaced with an alternative procedure to achieve lower background levels for application to gas-fired sources. In addition, probe designs (e.g., adding dilution air at the probe entrance through a section of porous or perforated tube wall) that reduce deposits to negligible levels, thereby eliminating the need to recover deposits from the probe, should be explored.

- Validation for Source Types. The method and equipment should be rigorously validated for measuring PM2.5 mass on different source types, using EPA Method 301 procedures as a guide. Specifically, a significant number of paired dilution sampler tests are needed to distinguish measurement and process variation for rigorous determination of

measurement precision. Generation of reference aerosols with known concentration also is recommended, with quantitative recovery of deposits from the various sections of the sampler, over a range of concentrations also is recommended.

- Validation for Species. Validated ambient air speciation methods were applied to the dilution sampler. Validation literature should be reviewed to determine whether further validation tests are needed to extend the results to sample matrices and concentrations in the diluted source samples. Further evaluation of OC measurements is strongly recommended for low concentration sources i.e. gas combustion. More detailed OC fractions should be reviewed from the current test program to determine if a different analytical protocol is justified.

Emission Factors and Speciation Profiles

- The current population of data for each source category is small, but is considered a good start toward developing robust emission factors and speciation profiles. Because of the small number of units tested (one to three), the emission factors may not be representative of either any individual unit or the entire population of units in each category (although this is frequently a limitation of many published emission factors). The high statistical uncertainty (typically in the range of approximately 40 to more than 100 percent) associated with many of the emission factors highlights the need for more tests to better understand and reduce sources of variability. Because it is likely that the emission factors for gas-fired units derived from these tests include a degree of positive bias due to measurement background levels that were demonstrated in some of the tests, the values may be considered conservatively high. Therefore, these emission factors and speciation profiles should be used with caution. Despite these limitations, the emission factors for gas-fired sources derived from dilution sampling are believed to be more representative than other published emission factors based on traditional methods for these sources (which in some cases may suffer from similar limitations) because of improved accuracy and differences in process configuration. Additional tests within each of the source categories evaluated in this program are needed after dilution method improvements and validation have been achieved.

REFERENCES

API. 2001a. Gas-Fired Boiler – Test Report Site A: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4703. American Petroleum Institute, Washington, D.C.

API. 2001b. Gas-Fired Heater – Test Report Site B: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4704. American Petroleum Institute, Washington, D.C.

API. 2001c. Gas-Fired Steam Generator – Test Report Site C: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4712. American Petroleum Institute, Washington, D.C.

Arunkumar, R., J. Etheridge, K. Hogancamp, J.C. Luthe, B.A. Nagel, O.P. Norton, M. Parsons, D. Rogers, C.A. Waggoner. 2004. "An Evaluation of EPA Reference Method 5I Accuracy," WM'04 Conference, Tucson, Arizona.

Brown, J.W. 1979. "Laboratory Tests for Investigation of Glass Beaker Weight Changes Following Desiccation," internal report (unpublished), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Carpenter, K.A. (1978). Master's Thesis, Michigan Technological University.

Chan, T. and M. Lippmann. 1977. "Particle Collection Efficiencies of Air Sampling Cyclones: An Empirical Theory," *Environ. Sci. Technol.* 11(4):377-382.

Chang, M.C. and England, G.C. 2004a. "Update: Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Chang, M.C. and England, G.C. 2004b. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Other Report: Pilot-Scale Dilution Sampler Design And Validation Tests (Laboratory Study)," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Chow, J.C., J.G. Watson, H. Kuhns, V. Etyemezian, D.H. Lowenthal, D. Crow, S.D. Kohl, J.P. Engelbrecht, M.C. Green. 2004. "Source Profiles for Industrial, Mobile, and Area Sources in the Big Bend Regional Aerosol Visibility and Observational Study," *Chemosphere* 54:185–208.

Dayton, D.P. and J.T. Bursey. 2001. "Source Sampling Fine Particulate Matter: Wood-Fired Industrial Boiler," EPA-600/R-01-106, U.S. Environmental Protection Agency, National Risk Management Research Laboratory Research Triangle Park, NC 27711.

England, G. C., B. Toby, and B. Zielinska. 1998. Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles. Publication No. 344, Health and Environmental Affairs Department, American Petroleum Institute, Washington, D.C.

England, G.C. 2004. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Impact Of Operating Parameters On Fine Particulate Emissions From Natural Gas-Fired Combined Cycle and Cogeneration Power Plants," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

England, G.C. and T.P. McGrath. 2004a. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Fine Particulate Test Protocol," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

England, G.C. and T.P. McGrath. 2004b. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for A Cogeneration Plant with Supplementary Firing, Oxidation Catalyst and SCR at Site Golf," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

England, G.C., S. Wien, T.P. McGrath, and D. Hernandez. 2004. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for a Combined Cycle Power Plant with Oxidation Catalyst and SCR at Site Echo," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Grosjean, D., and J.H. Seinfeld. 1989. "Parameterization of the formation potential of secondary organic aerosols." *Atmos. Environ*. **23**, 1733-1747.

Hamil, H.F. and R.E. Thomas. 1976. "Collaborative Study of Particulate Emissions Measurements by EPA Methods 2, 3, and 5 Using Paired Particulate Sampling Trains," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, EPA-600/4-76-014.

HEI. 2002. "Understanding The Health Effects Of Components Of The Particulate Matter Mix: Progress And Next Steps," *HEI Perspectives*, Health Effects Institute, Boston, Massachusetts.

Hernandez, D., Nguyen, Q and England, G.C. 2004. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for a Diesel Fuel-Fired Compression Ignition Reciprocating Engine with a Diesel Particulate Filter at Site Foxtrot," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Hildemann, L.M., G.R. Cass, and G.R. Markowski. 1989. A dilution stack sampler for organic aerosol emissions: Design, characterization, and field tests. *Aerosol Sci. and Technol.* 10:193-204.

Hildemann, L.M., G.R. Markowski and G.R. Cass. 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 25(4):744-759.

Hildemann, L. M., Klinedinst, D. B., Klouda, G. A., Currie, L. A. and Cass, G. R., 1994. Sources of urban contemporary carbon aerosol. *Environ. Sci. Technol.* 9:28.

Hodan, W. 2002. *Updates and Improvements to the SPECIATE Data and Program*. SPECIATE Expert Panel Meeting, Charlotte, NC. October 10, 2002. http://www.epa.gov/ttn/chief/conference/ei12/poster/hodan.pdf

Houck, J.E., J.A. Cooper, and E.R. Larson. Dilution sampling for chemical receptor source fingerprinting." Presented at the 75th Annual Meeting of the Air Pollution Control Association, New Orleans, LA, June 20-25, 1982.

ISO 8178. 1996a. "Reciprocating internal combustion engines–Exhaust emission measurement-Part 1: Test-bed measurement of gaseous and particulate exhaust emissions," International Standard ISO 8178-1, International Organization for Standards, Geneva, Switzerland.

ISO 8178. 1996b. "Reciprocating internal combustion engines–Exhaust emission measurement-Part 2: Measurement of gaseous and particulate exhaust emissions at site," International Standard ISO 8178-2, International Organization for Standards, Geneva, Switzerland.

Kirshstetter, T.W., C.E. Corrigan and T. Novakov. 2001. Laboratory and Field Investigation of the Adsorption of Gaseous Organic Compounds onto Quartz Filters. *Atmos. Environ*. 35:1663-1671.

Kittelson, D. 1998. "Nanoparticles and Engines," Technical Meeting on Mobile Source Aerosol Sampling and Measurement Techniques (February, 1998), U.S. Environmental Protection Agency, Ann Arbor, Michigan.

Kittelson, D. B., M. Arnold and W. F. Watts, Jr. 1999. "Review of Diesel Particulate Matter Sampling Methods: Final Report," University of Minnesota, Department of Mechanical Engineering, Center for Diesel Research, Minneapolis, MN.

Kittelson, D., W. Watts and J. Johnson. 2002. "Diesel Aerosol Sampling Methodology - CRC E-43," Final Report, Coordinating Research Council, Alpharetta, Georgia.

Kittelson, D. 2004. "Ultrafine and Nanoparticle Emissions: An Ongoing Challenge." CAPCOA Conference on Diesel—What the Future Holds, Diamond Bar, California.

Kleeman, M.J., J.J. Schauer, and G.R. Cass. 2000. "Size and Composition Distribution of Fine Particulate Matter Emitted from Motor Vehicles," *Environ. Sci. Technol.* 34:1132-1142.

Lanier, W.S. and G.C. England. 2004. "Technical Memorandum: Conceptual Model of Sources of Variability in Combustion Turbine particulate with aerodynamic diameter less than 10 µm (PM10) Emissions Data," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Lanier, W.S. and C.D. Hendrix. 2001. "Reference Method Accuracy and Precision (ReMAP): Phase 1 – Precision of Manual Stack Emission Measurements," Research Committee on Industrial and Municipal Waste, ASME International, Washington, D.C.

Lee, S.W.; Pomalis, R.; Kan, B. 2000. "A New Methodology for Source Characterization of Oil Combustion Particulate Matter;" *Fuel Process. Technol*. 65-66, 189-202.

Lee, S.W. 2001. "Source Profiles of Particulate Matter Emissions from a Pilot-Scale Boiler Burning North American Coal Blends," *J. Air & Waste Manage. Assoc*. 51:1568-1578.

Lee, S.W., I. He, T. Herage and B. Young. 2003. "Fine Particulate Matter Emission Research at CANMET Energy Technology Centre," PM Speciation Sub-group Meeting (Toronto, Canada), Environment Canada, Ottawa, Ontario, Canada.

Lighty, J.S., Veranth, J.M., and Sarofim, A.F. 2000. Combustion aerosols: Factors governing their size and composition and implications for human health. *J. Air & Waste Manage. Assoc*. 50:1565-1618.

Linder, G. and S. Wall. 1995. "Comparison of PAH emissions determined by ARB Method 429 and a dilution sampling (DS) method." Unpublished presentation to Engineering Foundation Conference on Stationary Source Sampling and Analysis for Air Pollutants XIX, San Diego, CA.

Lipsky, E., Stanier, C. O., Pandis, S. N., and Robinson, A. L. 2002. Effects of Sampling Conditions on the Size Distribution of Fine Particulate Matter Emitted from a Pilot-Scale Pulverized-Coal Combustor, *Energy Fuels* 16(2):302–310.

Mazurek, M.A., L.M. Hildemann, G.R. Cass, B.R.T. Simoneit, and W.F. Rogge. 1993. Methods of analysis for complex organic aerosol mixtures from urban emission sources of particulate carbon" in *Sampling and Analysis of Airborne Pollutants*, E.D. Winegar and L.H. Keith, eds., Lewis Publishers, Boca Raton, FL.

McDonald, J., Zielinska, B., Fujita, E., Chow, J., Watson, J., Sagebiel, J., Hayes, T., Sheetz, L. and Batie, S. 1998. Chemical Speciation of PM2.5 Emissions from Residential Wood Combustion and Meat Cooking. Air and Waste Management Association Specialty Conference on PM2.5: A Fine Particulate Standard, Long Beach, CA, January 1998.

Miller, C.A., W.P. Linak, C. King, J.O.L. Wendt. 1998. "Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler," *Combust. Sci. and Technol.* 134:477-502.

NRC. 1999. Research Priorities for Airborne Particulate Matter, II: Evaluation Research Progress and Updating the Portfolio. National Research Council. National Academy Press, Washington. D.C.

O'Connor, D. 2003. "PAPRICAN's Dilution Tunnel Development for the Pulp and Paper Sector," PM Speciation Sub-group Meeting (Toronto, Canada), Environment Canada, Ottawa, Ontario, Canada.

O'Connor, B. and S. Genest. 2003a. "PM10 and PM2.5 Emission from Pulp and Paper Mill Combustion Sources using a Dilution Tunnel Sampler," presented at TAPPI International Environmental Conference (May 5-7, 2003, Portland, Oregon), Technical Association of the Pulp and Paper Industry, Atlanta, Georgia.

O'Connor, B. and S. Genest. 2003b. "Development of PM10 and PM2.5 Stack Emission Factors for Kraft Mill Smelt Dissolving Tanks and Lime Kilns with Wet Scrubbers," presented at the PAPTAC Pacwest Conference (May 7-10, 2003, Harrison Hot Springs, B.C.), Pulp and Paper Technical Association of Canada, Montreal, Quebec, Canada.

Rigo, H.G. and A.J. Chandler. 1999. "Quantitation Limits for Reference Methods 23, 26 and 29," *J. Air & Waste Manage. Assoc*. 49:399-410.

Ryan, R. 2002. Speciation Profiles and Assignment Files Located on EMCH. Memorandum, U.S. EPA, Emission Factor and Inventory Group, Research Triangle Park, NC, March 8, 2002. http://www.epa.gov/ttn/chief/emch/speciation/emch_speciation_profile.pdf

Samaras, Z. 2002. "The EU DG TREN "Particulates" Project: Characterisation of Exhaust Particulate Emissions from Road Vehicles," CRC Workshop on Vehicle Exhaust Particulate Emission Measurement Methodology (San Diego, California), Coordinating Research Council, Alpharetta, Georgia.

Lighty, J.S., Veranth, J.M., and Sarofim, A.F. (2000) Combustion aerosols: Factors governing their size and composition and implications for human health. *J. Air & Waste Manage. Assoc*. 50:1565-1618..

Seinfeld, J.H. and Pandis, S.N., 1998. *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*, John Wiley & Sons, New York, NY.

Shigehara, R. 1996. "Minimum Detection Limit for Method 5," EPA Contract No. 68-D2-0163, Work Assignment 3-06, prepared by Entropy, Incorporated for U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

Smith, W. B., K.M. Cushing, J.W. Johnson, C.T. Parsons, A.D. Williamson, and R.R. Wilson, Jr. 1982. *Sampling and data handling methods for inhalable particulate sampling*." EPA-600/7-82-036, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Turpin, B.J., J.J. Huntzinger and S.V. Hering. 1994. Investigation of Organic Aerosol Sampling Artifacts in the Los Angeles Basin. *Atmos. Environ.* 34:2983-3013.

URG. 1996. *Model URG-3000R, Large source dilution sampling system – Operating Manual*. Prepared by URG, Chapel Hill, NC.

U.S. EPA. 1986. "Method 0020: Source Assessment Sampling System (SASS)," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Office of Solid Waste, Washington D.C. http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm, accessed October 21, 2004.

U.S. EPA. 1992. "Method 301: Field Validation of Pollutant Measurement Methods from Various Waste Media," Code of Federal Regulations, Title 40, Part 63, Appendix A, http://www.epa.gov/ttn/emc/promgate.html accessed October 21, 2004.

U.S. EPA. 1994. "Control of Emissions from New and In-Use Nonroad Compression-Ignition Engines," 59 FR 31335, U.S. Code of Federal Regulations, Title 40, Part 89.

U.S. EPA. 1996a. "Method 5 - Determination of Particulate Matter Emissions from Stationary Sources," Code of Federal Regulations, Title 40, Part 60, Appendix A, http://www.epa.gov/ttn/emc/promgate.html accessed October 21, 2004.

U.S. EPA. "1996b. "Method 201A - Determination of PM10 Emissions (Constant Sampling Rate Procedure)," Code of Federal Regulations, Title 40, Part 51, Appendix M, http://www.epa.gov/ttn/emc/promgate.html accessed October 21, 2004.

U.S. EPA. 1996c. "Method 202 - Determination of Condensible Particulate Emissions from Stationary Sources," Code of Federal Regulations, Title 40, Part 51, Appendix M, http://www.epa.gov/ttn/emc/promgate.html accessed October 21, 2004.

U.S. EPA. 1997a. "Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources," Code of Federal Regulations, Title 40, Part 60, Appendix A, http://www.epa.gov/hwcmact/frhwc5.pdf accessed October 21, 2004.

U.S. EPA. 1997b. Procedures for Preparing Emission Factor Documents (Revised). EPA-454/R-9-015, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

U.S. EPA. 2000b. "Guidance for Data Quality Assessment: Practical Methods for Data Analysis," EPA QA/G-9 (QA00 Update), EPA/600/R-96/084, Office of Environmental Information, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 2002a. "Conditional Test Method 040 – DRAFT Method for the Determination of PM10 And PM2.5 Emissions (Constant Sampling Rate Procedures)," http://www.epa.gov/ttn/emc/ctm.html accessed October 21, 2004.

U.S. EPA. 2002b. SPECIATE v3.2 Intro and User's Guide. November 1, 2002. http://www.epa.gov/ttn/chief/software/speciate/spec32_user_guide.txt.

U.S. EPA. 2002c. SPECIATE v3.2 Release Notes. November 1, 2002. http://www.epa.gov/ttn/chief/software/speciate/spec32_rel_notes.txt.

U.S. EPA. 2003a. "Measurement of PM 2.5 and PM 10 Emissions by Dilution Sampling (Constant Sampling Rate Procedures)," CTM-039, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. http://www.epa.gov/ttn/emc/ctm.html, accessed July 20, 2004.

U.S. EPA. 2003b. "Emissions Inventory Guidance for Implementation of Ozone and Particulate Matter National Ambient Air Quality Standards (NAAQS) and Regional Haze Regulations (Draft)," Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Wall, S.M. 1996. "Improved methods for PAH combustion source sampling." Final Report, California Air Resources Board Contract A932-098, NTIS PB97148746.

Warren, J. 2002. "Particle Attributes Associated with Toxicity," CRC Workshop on Vehicle Exhaust Particulate Emission Measurement Methodology (San Diego, California), Coordinating Research Council, Alpharetta, Georgia.

Watson, J.G., N.F. Robinson, C. Lewis and T. Coulter. 1997. Chemical Mass Balance Receptor Model Version 8 (CMB8) User's Manual. Desert Research Institute Document No. 1808.1D1 December, 1997.

Watson, J.G., J.C. Chow, D.H. Lowenthal, N.F. Robinson, C.F. Cahill, D.L Blumenthal. 2002. "Simulating Changes in Source Profiles from Coal-Fired Power Stations: Use in Chemical Mass Balance of PM2.5 in the Mount Zirkel Wilderness," *Energy & Fuels* 16:311-324.

Watson, J.G. and J. Chow. 2002. *Considerations in Identifying and Compiling PM and VOC Source Profiles for the SPECIATE Data Base*. SPECIATE Expert Panel Meeting, Charlotte, NC. October 10, 2002. http://www.epa.gov/ttn/chief/software/speciate/panel_minutes.zip.

Wien, S.E., G.C. England, K.R. Loos, K. Ritter. 2001. Investigation of Artifacts in Condensable Particulate Measurements for Stationary Combustion Sources. Paper #536. Air and Waste Management Association, 94th Annual Conference and Exhibition, Orlando, Florida, 25-27 June 2001.

Wien, S., England, G.C. and Chang, M.C. 2003. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for a Gas-Fired Process Heater (Site Alpha)," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C., http://www.nyserda.org/environment/emepreports.html accessed July, 2004.

Wien, S., England, G.C. and Chang, M.C. 2004a. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for A Combined Cycle Power Plant with Supplementary Firing, Oxidation Catalyst and SCR at Site Bravo," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Wien, S., England, G.C. and Chang, M.C. 2004b. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for a Gas-Fired Process Heater with Selective Catalytic Reduction (Site Charlie)," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C., http://www.nyserda.org/environment/emepreports.html accessed July, 2004.

Wien, S., England, G.C. and Chang, M.C. 2004c. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for Dual Fuel-Fired Commercial Boiler at Site Delta," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C., http://www.nyserda.org/environment/emepreports.html accessed July, 2004.

APPENDIX A LIST OF ABBREVIATIONS

<	less than (upper estimate of true emission)
°C	degrees Celsius
µg	micrograms
µm	micrometers (microns)
Al	aluminum
AMDL	analytical method detection limit
AMS	ambient monitoring station
API	American Petroleum Institute
As	arsenic
ASME	American Society of Mechanical Engineers
Ba	barium
Br	bromine
Ca	calcium
CalTech	California Institute of Technology
cc	cubic centimeter
CEC	California Energy Commission
Cl^-	chloride ion
Co	cobalt
CO	carbon monoxide
CNC	condensation nuclei counter
Cr	chromium
Cu	copper
DI	distilled deionized
DMA	differential mobility analyzer
DPF	Diesel particulate filter
DOE	United States Department of Energy
DRI	Desert Research Institute
DSB	dilution system blank
dscm	dry standard cubic meters
EC	elemental carbon
EPA	Environmental Protection Agency
Fe	iron
g	gram
g/cc	gram per cubic centimeter
Ga	gallium
GE	General Electric
GE EER	GE Energy and Environmental Research Corporation
GRI	Gas Research Institute
H_0	null hypothesis
H_2SO_4	sulfuric acid
HEPA	high efficiency particulate arrest (filter)
ISO	International Organization for Standardization
K	potassium
kg	kilograms

La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds per million British thermal units
L/min	liters per minute
LQL	lower quantification limits
MDL	method detection limit
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
mL	milliliter
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
NAAQS	National Ambient Air Quality Standards
NETL	National Energy Technology Laboratory
NH_3	ammonia
NH_4^+	ammonium ion
Ni	nickel
NO	nitric oxide
NO_3^-	nitrate ion
NO_x	nitrogen oxides
nm	nanometer
NYSERDA	New York State Energy Research and Development Authority
O_2	molecular oxygen
OC	organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbons
Pb	lead
PM	particulate matter
PM10	particulate with aerodynamic diameter of 10 micrometers and smaller
PM2.5	particulate with aerodynamic diameter of 2.5 micrometers and smaller
ppmw	parts per million by weight
QA/QC	quality assurance/quality control
QFF	quartz fiber filter
SASS	source assessment sampling system
SMPS	scanning mobility particle sizer
SCR	selective catalytic reduction
Si	silicon
SO_2	sulfur dioxide
$SO_4^=$	sulfate ion
Sr	strontium
SVOC	semivolatile organic compound
TC	total carbon
Ti	titanium
Tl	thallium
TMF	Teflon®-membrane filter
TOR	thermal/optical reflectance

TSI	Thermo Scientific Incorporated
ULPA	ultra-low penetrating air (filter)
V	vanadium
VOC	volatile organic compound
VOC^{8+}	volatile organic compounds with carbon number of 8 or more
WRPS	wide range particle spectrometer
Y	yttrium
Zr	zirconium

APPENDIX B SI CONVERSION FACTORS

	English (US) units	X	Factor	=	SI units
Area:	1 ft^2	x	9.29×10^{-2}	=	m^2
	1 in^2	x	6.45	=	cm^2
Flow Rate:	1 gal/min	x	6.31×10^{-5}	=	m^3/s
	1 gal/min	x	6.31×10^{-2}	=	L/s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.54×10^{2}	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft^3	x	28.3	=	L
	1 ft^3	x	0.0283	=	m^3
	1 gal	x	3.785	=	L
	1 gal	x	3.785×10^{-3}	=	m^3
Temperature	°F-32	x	0.556	=	°C
	°R	x	0.556	=	K
Energy	Btu	x	1055.1	=	Joules
Power	Btu/hr	x	0.29307	=	Watts